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# Microwave Plasma-Activated Chemical Vapor Deposition of Nitrogen-Doped Diamond. I. $\text{N}_2/\text{H}_2$ and $\text{NH}_3/\text{H}_2$ Plasmas

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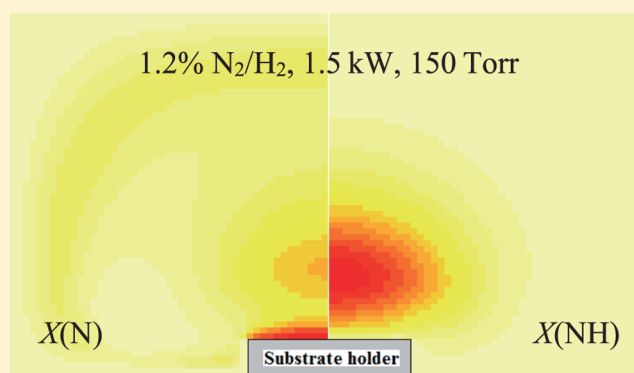
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**ABSTRACT:** We report a combined experimental/modeling study of microwave activated dilute  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  plasmas as a precursor to diagnosis of the  $\text{CH}_4/\text{N}_2/\text{H}_2$  plasmas used for the chemical vapor deposition (CVD) of N-doped diamond. Absolute column densities of  $\text{H}(n=2)$  atoms and  $\text{NH}(\text{X}^3\Sigma^-, v=0)$  radicals have been determined by cavity ring down spectroscopy, as a function of height ( $z$ ) above a molybdenum substrate and of the plasma process conditions, i.e., total gas pressure  $p$ , input power  $P$ , and the nitrogen/hydrogen atom ratio in the source gas. Optical emission spectroscopy has been used to investigate variations in the relative number densities of  $\text{H}(n=3)$  atoms,  $\text{NH}(\text{A}^3\Pi)$  radicals, and  $\text{N}_2(\text{C}^3\Pi_u)$  molecules as functions of the same process conditions. These experimental data are complemented by 2-D ( $r, z$ ) coupled kinetic and transport modeling for the same process conditions, which consider variations in both the overall chemistry and plasma parameters, including the electron ( $T_e$ ) and gas ( $T$ ) temperatures, the electron density ( $n_e$ ), and the plasma power density ( $Q$ ). Comparisons between experiment and theory allow refinement of prior understanding of N/H plasma-chemical reactivity, and its variation with process conditions and with location within the CVD reactor, and serve to highlight the essential role of metastable  $\text{N}_2(\text{A}^3\Sigma_u^+)$  molecules (formed by electron impact excitation) and their hitherto underappreciated reactivity with H atoms, in converting  $\text{N}_2$  process gas into reactive  $\text{NH}_x$  ( $x=0-3$ ) radical species.



## 1. INTRODUCTION

One of the key classifiers of natural diamonds is their nitrogen impurity content.<sup>1</sup> Nitrogen is the dominant impurity in type I diamonds, where it is typically present at the  $\sim 0.1$  atom % level. These constitute  $\approx 98\%$  of all natural diamonds and are traditionally further subdivided according to the way in which the nitrogen impurities are distributed within the carbon lattice (e.g., as isolated atoms, or aggregated as larger clusters), but all exhibit characteristic absorption features in the infrared (IR) and ultraviolet (UV), and visible fluorescence under UV illumination. Type II diamonds contain much lower N impurity levels (too low to be revealed by IR absorption spectroscopy) and are much rarer in nature. Natural type IIa diamonds are both very scarce and particularly prized, as they are almost entirely devoid of impurities and, as a result, are essentially colorless and display the highest thermal conductivity.

In contrast, given minimal air leakage into the reaction chamber and sufficiently pure process gases, diamonds grown by chemical vapor deposition (CVD) can be produced with very low nitrogen content, and are thus normally type IIa material. For example, Tallaire et al.<sup>2</sup> reported single-crystal

homoepitaxial growth of diamond with total defect concentrations  $< 200$  ppb using high-purity  $\text{CH}_4/\text{H}_2$  gas mixtures and a high-power-density microwave (MW) plasma process. These workers also showed that even trace (2–10 ppm) additions of  $\text{N}_2$  to the  $\text{CH}_4/\text{H}_2$  process gas mixture caused a substantial (up to 2.5-fold) increase in growth rate,<sup>2</sup> reinforcing and extending earlier<sup>3</sup> and subsequent<sup>4,5</sup> studies that demonstrate growth rate enhancements at higher nitrogen atom input mole fraction,  $X_0(\text{N})$ . Careful studies of CVD growth on synthetic (100) high-pressure, high-temperature (HPHT) single-crystal diamond substrates by Achard et al.<sup>6</sup> served to illustrate not just the evolution in growth mechanism, from a unidimensional (step flow) to a bidimensional nucleation mode, upon increasing  $X_0(\text{N})$ , but also the interdependence of diamond deposition rate, growth mechanism (hence morphology), and substrate temperature.

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Here we report the first in a sequence of studies designed to provide an in-depth analysis and understanding of the roles of nitrogen in diamond CVD. The presence of nitrogen in MW-activated  $\text{CH}_4/\text{H}_2$  plasmas can be traced by optical emission spectroscopy (OES). Several previous studies have reported the variation in  $\text{CN}(\text{B}-\text{X})$  emission intensity upon varying  $X_0(\text{N})$  in  $\text{CH}_4/\text{H}_2$  plasmas,<sup>3,7,8</sup> but quantifying the CN number density is much harder, and it remains to be established what measurements of relative CN emission intensities (normally from the plasma core) tell one about the densities of the various different N-containing species near the growing diamond surface.

This question will be addressed in a future publication (paper II), via spatially resolved absolute and relative density measurements of  $\text{H}(n = 2, 3)$  atoms, CH, NH,  $\text{C}_2$ , and CN radicals, and metastable triplet  $\text{N}_2$  molecules in MW-activated  $\text{CH}_4/\text{N}_2/\text{H}_2$  gas mixtures, using a combination of absorption (cavity ring down) spectroscopy (CRDS) and OES.<sup>9</sup> These data will be discussed and interpreted in light of complementary two-dimensional (2-D ( $r, z$ ), where  $r$  and  $z$  are, respectively, the radial distance and the vertical height from the center of the substrate surface) modeling<sup>10</sup> of the C/N/H plasma chemistry and composition as a function of process conditions, i.e.,  $\text{CH}_4$  and  $\text{N}_2$  fractions, total pressure  $p$ , and applied MW power  $P$ . Such analysis returns absolute number density estimates for the more abundant N-containing radical species, such as  $\text{NH}_x$  ( $x = 0-2$ ) and CN radicals, in the immediate vicinity of a growing diamond surface. The results can then be used to inform models of elementary reaction sequences, whereby such species can add to, and migrate on, a diamond (100) surface, as modeled using a mixture of quantum and molecular mechanical (QM and QM/MM) methods. This gas-surface chemistry modeling work will form the basis of a future third paper in this series (paper III).<sup>11</sup>

The present paper (paper I) reports spatially resolved absorption and/or emission measurements of  $\text{H}(n = 2, 3)$  atoms, NH radicals, and triplet  $\text{N}_2$  molecules in MW-activated  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  plasmas operating at pressures ( $\sim 150$  Torr) and powers ( $\sim 1.5$  kW) relevant to commercial MW plasma-activated (PA) CVD reactors. These results inform and tension companion 2-D modeling of the N/H plasma chemistry, and represent an essential precursor to the detailed analysis of MW-activated C/N/H plasmas reported in paper II.  $\text{N}_2/\text{H}_2$  plasmas have been studied previously, in low-pressure direct current (dc)<sup>12</sup> and MW<sup>13</sup> discharges, and at higher pressures in an expanding arc reactor,<sup>14,15</sup> but we are not aware of any quantitative investigations at the conditions of pressure, temperature, and electron density normally prevailing in MW-PACVD reactors used for diamond growth.

## 2. EXPERIMENTAL METHODS

The MW-PACVD reactor, the laser system, and the optical arrangements for the spatially resolved CRDS measurements as a function of height ( $z$ ) above the substrate surface have been described elsewhere.<sup>16</sup> CRDS was used to determine absolute column densities of electronically excited  $\text{H}(n = 2)$  atoms (monitoring the  $n = 3 \leftarrow n = 2$  Balmer- $\alpha$  transition)<sup>17</sup> and ground state  $\text{NH}(\text{X}^3\Sigma^-, v = 0)$  radicals (using selected lines within the  $\text{A}^3\Pi-\text{X}^3\Sigma^-$  system, as in our previous study of hot filament-activated  $\text{NH}_3$ -containing C/N/H gas mixtures).<sup>18</sup> The previously described optical setup for OES measurements<sup>19</sup> was revised for the present work, with a simple Keplerian telescope arrangement providing greatly enhanced

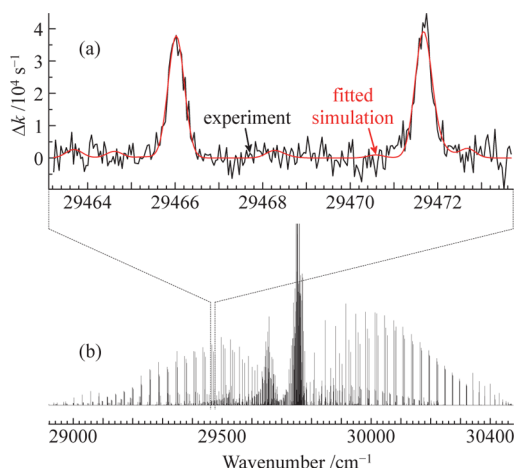
light-gathering ability relative to the prior approach. With the trade-off of spatial resolution (now  $\approx 3$  mm) for improved spectral resolution (now 0.15 nm fwhm) and signal-to-noise ratio, partially rotationally resolved UV emission spectra were obtained that show detailed (but strongly overlapped) rovibronic structure due to  $\text{N}_2$  and NH (and, in the case of C/N/H plasmas, also CN and CH) radicals, as described below. The  $\text{N}_2$  and NH OES data reported here and in paper II were all taken with the spectrometer transmission centered at  $\approx 336$  nm. Though not important for N/H plasmas, this choice is crucial in the case of C/N/H plasmas since it avoids the much stronger CN, CH, and  $\text{C}_2$  emissions lying further to the red, which would otherwise limit the maximum possible integration time before detector saturation and thus render our measurements insufficiently sensitive toward  $\text{N}_2$  and NH. An important difference with respect to the previous configuration<sup>19</sup> is that the present OES measurements are sampled from a volume nominally at the radial center of the plasma, rather than attempting to emulate the line-integrated sampling mode of CRDS.

The  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  source gases were introduced through separate, calibrated mass flow controllers (MFCs), and mixed prior to entering the reactor through two diametrically opposed inlets located close below the fused silica window (which constitutes the top of the reactor), at an angle of  $\approx 45^\circ$  to the probe axis. “Base” conditions for the experimental studies were defined as follows: total pressure  $p = 150$  Torr, input power  $P = 1.5$  kW, and input flow rates  $F(\text{N}_2) = 3$  standard  $\text{cm}^3$  per minute (sccm) for OES measurements or 6 sccm for CRDS,  $F(\text{NH}_3) = 6$  sccm, and  $F(\text{H}_2) = 500$  sccm. When one parameter was varied, all others were maintained at their base values, except where noted. The substrate temperature  $T_{\text{sub}}$  was monitored using a two-color optical pyrometer operating in the wavelength range 700–1000 nm, which indicated a higher value ( $\approx 1100$  K) under base conditions than the  $\approx 973$  K estimated by one-color pyrometry as used in our previous work.<sup>10</sup> We consider the new value more reliable due to its independence of an (usually problematic) estimate of substrate emissivity, which is itself a function of temperature as well as sensitively dependent on surface condition.

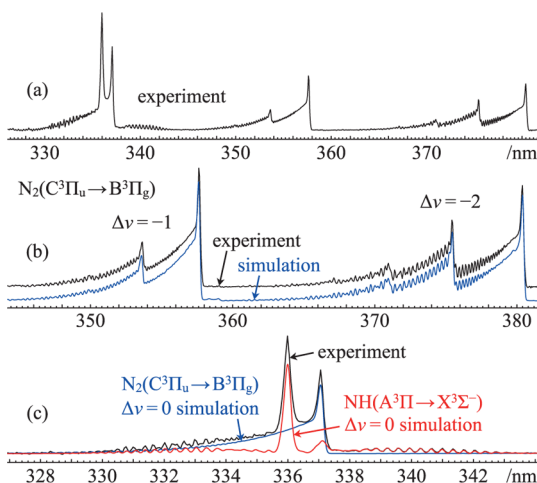
## 3. EXPERIMENTAL RESULTS

Figure 1a shows a CRDS measurement of a small part of the  $\text{NH}(\text{A}^3\Pi-\text{X}^3\Sigma^-) \Delta v = 0$  band system obtained at  $z = 8$  mm from a  $\text{N}_2/\text{H}_2$  plasma operating under base conditions. Given literature values for the relevant spectroscopic constants<sup>20</sup> and Franck-Condon factors,<sup>21,22</sup> a simulation (as shown in the figure) can be constructed using PGOPHER<sup>23</sup> that provides assignments for rotational lines originating from the  $v'' = 0$  and  $v'' = 1$  vibrational levels, and which may be fitted to the experimental spectrum to recover absolute column densities. Both the fitted simulation and that of the complete  $\text{NH}(\text{A}-\text{X}) \Delta v = 0$  progression, shown in Figure 1b, assume rotational and vibrational temperatures ( $T_{\text{rot}}$  and  $T_{\text{vib}}$ ) of 2900 K.

The optical emission spectrum displayed in Figure 2a spans a much wider ( $\approx 50$  nm) wavelength range, and reveals not just the  $\text{NH}(\text{A}-\text{X}) \Delta v = 0$  band system at  $\approx 336$  nm, but also progressions of vibronic bands associated with the second positive ( $\text{C}^3\Pi_u-\text{B}^3\Pi_g$ ) system of  $\text{N}_2$ .<sup>24,25</sup> Figure 2b,c shows expanded views of parts of this system. The former shows the  $\text{N}_2(\text{C}-\text{B}) \Delta v = -1$  and  $\Delta v = -2$  progressions along with a PGOPHER simulation using the appropriate spectroscopic constants,<sup>24</sup> while the latter illustrates the separation of the



**Figure 1.** Part of the  $\text{NH}(\text{A}-\text{X})$   $\Delta v = 0$  band system (a) as measured by CRDS at  $z = 8$  mm in a  $\text{N}_2/\text{H}_2$  (6/500 sccm) plasma operating under base conditions, with fitted PGOPHER simulation at fixed  $T_{\text{rot}} = T_{\text{vib}} = 2900$  K, and (b) shown in the context of the complete (simulated) progression, illustrating the overlapping  $\nu' - \nu'' = 0-0, 1-1,$  and  $2-2$  bands.



**Figure 2.** Optical emission spectra, measured at  $z = 7$  mm, of a MW-activated  $\text{N}_2/\text{H}_2$  (9/500 sccm) mixture operating otherwise under base conditions. (a) Overview spectrum showing the  $\text{NH}(\text{A}-\text{X})$   $\Delta v = 0$  band system centered at  $\approx 336$  nm, along with three progressions of bands from the second positive ( $\text{C}^3\Pi_u - \text{B}^3\Pi_g$ ) system of  $\text{N}_2$ . Panel (b) shows an expanded view of the  $\text{N}_2(\text{C}-\text{B})$   $\Delta v = -1$  and  $\Delta v = -2$  progressions, while part (c) illustrates the overlapping  $\text{N}_2(\text{C}-\text{B})$   $0-0$  band and  $\text{NH}(\text{A}-\text{X})$   $\Delta v = 0$  progression. Both are shown together with a common PGOPHER simulation, vertically offset for clarity in part (b), using the appropriate spectroscopic constants and with respective rotational temperatures treated as parameters and varied for best fit.

overlapping  $\text{N}_2(\text{C}-\text{B})$   $(0,0)$  band and  $\text{NH}(\text{A}-\text{X})$   $\Delta v = 0$  progression, which must be accomplished with high fidelity<sup>26</sup> in order to track the variation in emission intensity for each species with  $z$  and/or process conditions. For brevity, the  $\text{N}_2(\text{C}-\text{B})$   $(0,0)$  and  $\text{NH}(\text{A}-\text{X})$   $(0,0)$  band emissions, the intensities of which we consider representative and report exclusively in the remainder of this work, will henceforth be referred to simply as  $\text{N}_2^*$  and  $\text{NH}^*$ . Spectra recorded at longer wavelengths showed the usual intense H Balmer series emission<sup>19</sup> (henceforth  $\text{H}^*$ ), but no detectable emissions from atomic nitrogen, even when  $X_0(\text{N})$  was raised to 30%.

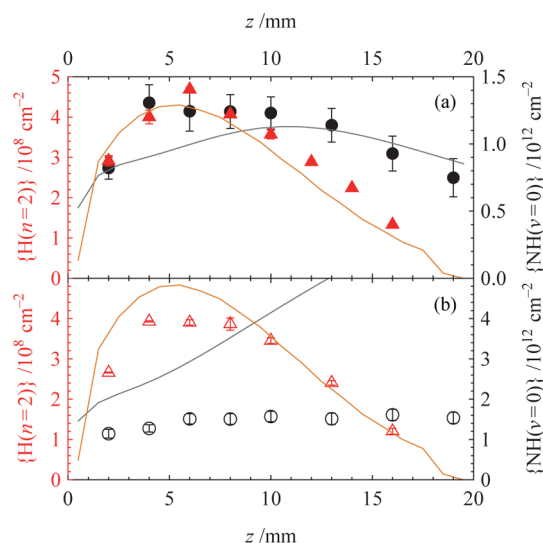
The various multiplets associated with the  $2p^23p^1 \rightarrow 2p^23s^1$  transition of N lying near 744, 820, and 865 nm all possess large A-coefficients ( $\approx 10^7 \text{ s}^{-1}$ )<sup>27–29</sup> and occur in a wavelength range for which our detection is relatively more sensitive than in the UV. Thus, they should be readily observable if the  $\text{N}(2p^23p^1)$  densities were comparable to those of the other species, but this is far from the case.<sup>30</sup>

OES is a valuable technique for determining variations in relative species concentration with changes in process parameters, providing that the latter changes have minimal confounding influence on that part of the electron energy distribution responsible for exciting the optical emission. CRDS, in contrast, provides absolute column densities. The procedure for obtaining  $\text{H}(n=2)$  column densities from CRDS measurements on the  $n=3 \leftarrow n=2$  Balmer- $\alpha$  transition is unchanged from that used in our previous studies,<sup>16</sup> and so is not repeated here. The experimental measurable is the change in ring down rate ( $\Delta k, \text{s}^{-1}$ ) versus wavenumber ( $\bar{\nu}, \text{cm}^{-1}$ ). For a radical species such as NH, eq 1 provides the link from CRDS measurements of an individual spectral line to the absolute column density, which we notate as, e.g.,  $\{\text{NH}(\nu=0)\}$ :

$$\{\text{NH}(\nu=0)\} = \frac{8\pi L \bar{\nu}^2 g_l}{A p_{\text{line}} g_u} \int_{\text{line}} \Delta k \, d\bar{\nu} \quad (1)$$

Here,  $L$  is the length of the cavity (92 cm),  $g_l$  and  $g_u$  are the degeneracies of the  $\text{X}^3\Sigma^-$  and  $\text{A}^3\Pi$  states (3 and 6, respectively), and  $A$  is the Einstein A-coefficient for the  $(0,0)$  band of the  $\text{A}-\text{X}$  transition. In the present work,  $A$  has been taken as  $\approx 2.44 \times 10^6 \text{ s}^{-1}$  per ref 21, although it should be noted that other similar values have been given in the more recent ref 22 and references therein.  $p_{\text{line}}$  is the ratio of the integrated intensity of the spectral line under study to the total band intensity, which is calculated assuming that the NH radicals are localized in a volume of reasonably constant gas temperature,  $T$ . Given the collision frequency at the pressures of interest, and informed by rotational temperatures obtained by fitting to the observed band contour of the  $\text{NH}^*$  optical emission spectrum, we assume  $T_{\text{gas}} = T_{\text{rot}} = T = 2900 \pm 300$  K, and hence calculate  $p_{\text{line}}$  using PGOPHER and the relevant spectroscopic constants,<sup>20,21</sup> with the total band intensity obtained as the integrated intensity over all rotational lines within the  $(0,0)$  band. The calculated  $p_{\text{line}}$  values for the lines contributing to the simulation shown in Figure 1 are  $5.44(12) \times 10^{-3}$ ,  $4.81(11) \times 10^{-3}$ , and  $1.07(7) \times 10^{-3}$  for the  $(0,0)$   ${}^{\text{P}}\text{P}_1(10)$  (29 466.02  $\text{cm}^{-1}$ ),  $(0,0)$   ${}^{\text{Q}}\text{P}_{32}(9)$  (29 471.65  $\text{cm}^{-1}$ ), and  $(1,1)$   ${}^{\text{P}}\text{P}_1(7)$  (29 471.80  $\text{cm}^{-1}$ ) lines, respectively, where the quoted uncertainties are due to the range of  $T$  considered. Given the experimental resolution ( $\approx 0.3 \text{ cm}^{-1}$  fwhm), the latter two lines are unresolved, and line-integrated  $\Delta k$  values were obtained by simultaneously fitting one (assumed Gaussian) profile to the  ${}^{\text{P}}\text{P}_1(10)$  line, and another of equal width to the sum of the other two lines, with the relative area of the latter fixed to its temperature-determined value of 0.925(15). From these three lines we hence recovered “ ${}^{\text{P}}\text{P}_1(10)$ -equivalent” values of  $\Delta k$ , from which column densities were calculated using the corresponding  $p_{\text{line}}$ . The choice of lines was guided partly by the uncertainty in temperature, and thus minimal variation of the relative intensities was sought: the values of  $p_{\text{line}}$  and the intensity ratio, even including implausibly high (3600 K) and low (2200 K) average temperatures, span the fairly narrow ranges  $5.02 \times 10^{-3}$ – $5.74 \times 10^{-3}$  and 0.884–0.980, respectively, for the lines used in the present analysis.



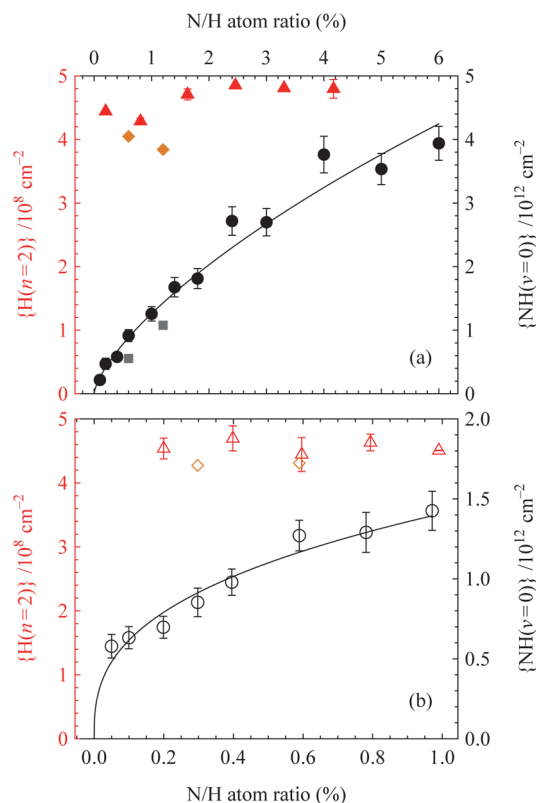


**Figure 3.** Profiles of  $\{NH(v=0)\}$  (black circles) and  $\{H(n=2)\}$  (red triangles) with respect to  $z$  obtained by CRDS probing of (a)  $N_2/H_2$  (6/500 sccm, filled symbols) and (b)  $NH_3/H_2$  (6/500 sccm, open symbols) plasmas operating under base conditions. The gray and orange lines are calculated  $\{NH(v=0)\}$  and  $\{H(n=2)\}$  profiles, respectively.

Figure 3a,b shows  $z$ -dependent profiles for  $\{H(n=2)\}$  and  $\{NH(v=0)\}$  as measured by CRDS in  $N_2/H_2$  and  $NH_3/H_2$  plasmas, respectively, operating under base conditions. The  $\{H(n=2)\}$  profiles in these dilute N/H plasmas appear insensitive to the choice of nitrogen precursor, and are reminiscent of those reported previously when using dilute  $C/H/(Ar)^{16}$  and  $C/H/O^{17}$  gas mixtures in this same reactor, peaking at  $z \approx 6$  mm and decreasing both toward the substrate and (less steeply) at larger  $z$ . The  $\{NH(v=0)\}$  distribution is clearly more extensive in both cases, and the measured  $\{NH(v=0)\}$  values in the two plasmas are very similar despite the approximately 2-fold difference in  $X_0(N)$  between the two precursor gases for any given flow rate.

Figure 4 shows measured variations in  $\{H(n=2)\}$  and  $\{NH(v=0)\}$  at  $z = 8$  mm with changing  $X_0(N)$  for (a)  $N_2/H_2$  and (b)  $NH_3/H_2$  plasmas. The results are presented with respect to N/H atom ratio, defined in terms of the flow rates as  $F(N_2)/F(H_2)$  and  $F(NH_3)/[3F(NH_3) + 2F(H_2)]$ , respectively, depending on the N precursor. We further note that  $X_0(N)$  and the N/H atom ratio are almost equal for small nitrogen additions.  $\{H(n=2)\}$  appears insensitive to small additions of  $N_2$  or  $NH_3$ , while  $\{NH(v=0)\}$ , unsurprisingly, increases with  $X_0(N)$ . The rate of increase is less than directly proportional in both cases, with the rate of rise diminishing as  $X_0(N)$  further increases. A sharp rise of  $\{NH(v=0)\}$  for  $F(NH_3) < 1$  sccm can be inferred from the zero-offset observed in Figure 4b, which contrasts with the roughly linear trend seen for small  $F(N_2)$ . The continuous curves drawn through the data points are power laws of the form  $\text{const} \times X_0(N)^a$ , with best-fitting exponents (a)  $a = 0.70$  and (b)  $a = 0.36$ . We discuss the interpretation of these values in the following section.

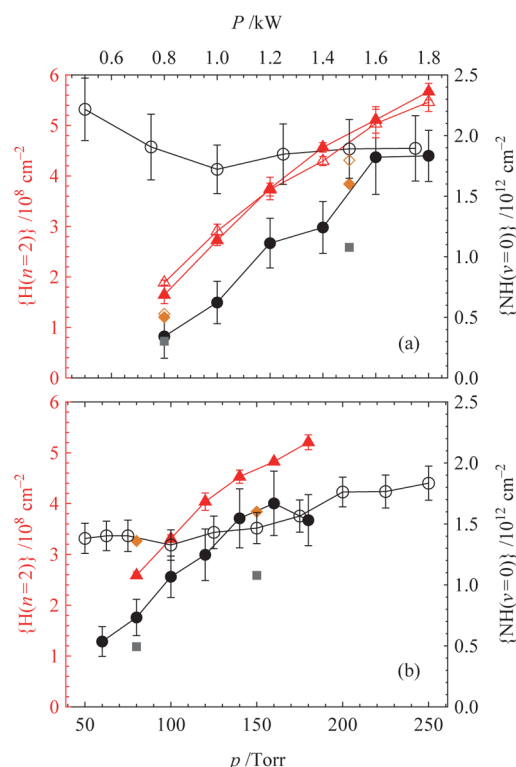
Column density variations with power and pressure, again measured at  $z = 8$  mm, with all other parameters maintained at their base values, are shown in Figure 5. The  $\{NH(v=0)\}$  versus  $P$  plot, Figure 5a, clearly demonstrates sensitivity to the choice of nitrogen precursor. In the case of the  $N_2/H_2$  plasma,  $\{NH(v=0)\}$  increases approximately 4-fold as  $P$  is raised from



**Figure 4.** Variations in  $\{H(n=2)\}$  and  $\{NH(v=0)\}$  for (a)  $N_2/H_2$  and (b)  $NH_3/H_2$  plasmas plotted as a function of N/H ratio in the input gas mixture (defined on the top and bottom horizontal axes, respectively). Both plasmas operated otherwise at base conditions and were probed at  $z = 8$  mm. The symbol key is as in Figure 3. The black lines are curves of the form  $\{NH(v=0)\} \sim X_0(N)^a$ , with best-fitting exponents of (a)  $a = 0.70$  and (b)  $a = 0.36$ . The gray squares and orange diamonds show calculated values of  $\{NH(v=0)\}$  and  $\{H(n=2)\}$ , respectively, under the given conditions. The calculated  $\{NH(v=0)\}$  values for the  $NH_3/H_2$  plasma (not shown) are roughly twice the experimental values, as discussed in the text.

0.8 to 1.8 kW, whereas the same increase in  $P$  in the case of  $NH_3/H_2$  leads to a modest reduction in  $\{NH(v=0)\}$ . The value of  $\{NH(v=0)\}$  is, however, consistently greater in the  $NH_3/H_2$  plasma for all powers, even though  $X_0(N)$  is only one-quarter of that for the corresponding  $N_2/H_2$  plasma. Changes in pressure have an effect roughly analogous to those of power: as seen in Figure 5b,  $\{NH(v=0)\}$  largely follows  $\{H(n=2)\}$  in the  $N_2/H_2$  mixture, but shows only weak dependency on either variable when using  $NH_3$  as the N source gas. We emphasize, however, that the trends shown in Figure 5 reflect the changing size and power density of the plasmas as well as their local compositions and parameters, so that physical interpretation must necessarily rely in large part on the complementary modeling studies.

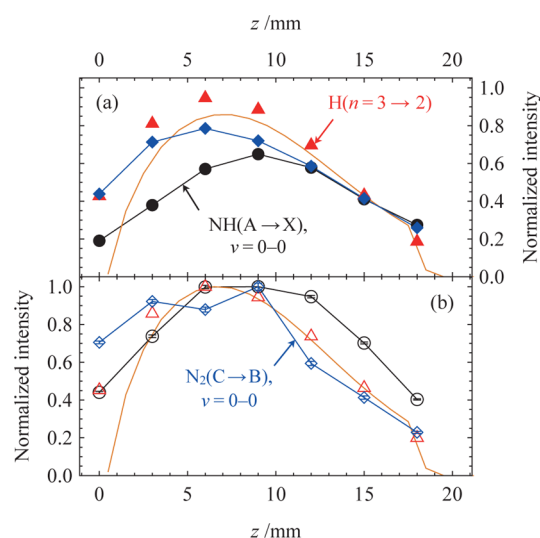
OES measurements show many of the same trends. Spatial profiles of the  $H^*$  emission from the  $N_2/H_2$  and  $NH_3/H_2$  plasmas (Figures 6a,b, respectively) are very similar to each other and, peaking at  $z \approx 6$  mm, have overall envelopes comparable to those given in Figure 3 for  $\{H(n=2)\}$  as measured by CRDS. The  $N_2^*$  emission spatial profile closely resembles that of  $H^*$ . It should be noted that the relative emission intensities given for  $z = 0$  mm are consistently and necessarily underestimates relative to the other spatial locations, since the substrate (rather than the plasma) then fills the lower



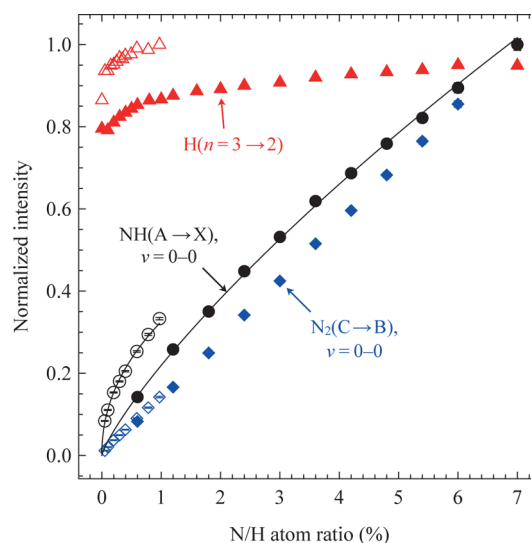
**Figure 5.** Variations in  $\{H(n=2)\}$  and  $\{NH(v=0)\}$ , probed at  $z = 8 \text{ mm}$ , with respect to (a) applied MW power and (b) pressure. The plasmas were maintained otherwise at base conditions, with flows of 6/500 sccm for both the  $N_2/H_2$  and  $NH_3/H_2$  mixtures. The symbol key is as in Figure 4, with filled and open symbols for the  $N_2/H_2$  and  $NH_3/H_2$  plasmas, respectively. Points in each series are joined by straight line segments for visual clarity. Calculated  $\{H(n=2)\}$  and  $\{NH(v=0)\}$  values are again indicated with orange diamonds and gray squares, respectively, and the latter values for the  $NH_3/H_2$  plasma are off scale and thus not shown.

half of the imaged region; CRDS measurements, in contrast, are impossible with the substrate partially occluding the beam path. The shapes of the  $NH^*$  emission profiles are insensitive to the choice of nitrogen source, but peak at larger  $z$  than the  $H^*$  profiles, which is again consistent with the CRDS measurements of  $\{NH(v=0)\}$ . In both plasmas, the  $NH^*/N_2^*$  emission ratio increases approximately 2-fold across the range  $z = 0$  to 18 mm, reflecting this more extensive  $NH$  distribution.

The measured  $NH^*$  emission from the  $NH_3/H_2$  plasma is more intense than that from the equivalent  $N_2/H_2$  plasma. So, too, is the  $N_2^*$  emission. The former observation may be explained, at least partially, by the finding from CRDS that the (ground state)  $NH$  density is greater for  $NH_3$  additions than with the same  $X_0(N)$  from  $N_2$ , but the latter also implies some contribution from increased electron density  $n_e$  and/or temperature  $T_e$  in the  $NH_3/H_2$  case. This finding is illustrated more clearly in Figure 7, which shows the scaling of the emission intensities with  $N/H$  atom ratio for both plasmas. The  $H^*$  emission shows a small, but sharp, increase upon small additions of  $NH_3$ , and a similar but more gradual increase when using  $N_2$ , while no comparable effect was seen for  $\{H(n=2)\}$  in Figure 4a; any differences in the  $N_2^*$  emission intensities are hard to discern. The small increases in  $H^*$  and the linear increase in  $N_2^*$  emission intensity imply that increasing  $X_0(N)$  in the source gas mixture causes only minor variations in the plasma parameters. Such variations as are observed could reflect



**Figure 6.**  $z$ -profiles of  $H^*$ ,  $NH^*$ , and  $N_2^*$  emissions from (a)  $N_2/H_2$  (3/500 sccm) and (b)  $NH_3/H_2$  (6/500 sccm) plasmas, both operating under base conditions. The emission intensities displayed in both panels are mutually normalized, for each species, to the maximal value measured at any  $z$  from either plasma. The symbol key is as in the previous figures, with the addition of blue diamonds for  $N_2^*$ . The orange lines show calculated  $H(n=3)$  (relative) concentrations at  $r = 0$  as a function of  $z$  for the respective plasmas, and match well with the measured  $H^*$  emission profiles. The points in the  $NH^*$  and  $N_2^*$  profiles are joined with straight line segments for visual clarity.

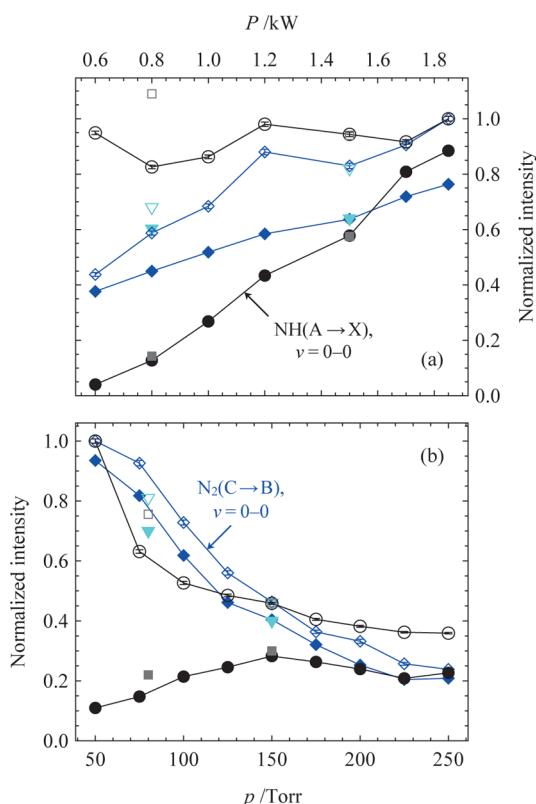


**Figure 7.**  $H^*$ ,  $NH^*$ , and  $N_2^*$  emission intensities measured at  $z = 7 \text{ mm}$  for  $N_2/H_2$  (filled symbols) and  $NH_3/H_2$  (open symbols) plasmas, both operating under otherwise base conditions, plotted as a function of  $N/H$  ratio in the input gas mixture. Symbols are as in Figure 6. Emission intensities are normalized to the maximum value observed for each species, and flow rates of the respective nitrogen precursors are expressed as  $N/H$  atom ratios. The black lines are curves of the form  $NH^* \sim X_0(N)^a$ , with best-fitting exponents of  $a = 0.81$  in the  $N_2/H_2$  case and  $a = 0.47$  for  $NH_3/H_2$ .

changes in the dominant ion(s) and in electron–ion recombination rates and/or minor changes of the maximum gas temperature  $T_{\text{max}}$  and  $T_e$ . We return to this issue in section 4, but the similar  $N_2^*$  emission intensities, and the fact that this quantity scales essentially directly proportionally to the input  $N/H$  atom ratio, both suggest that the strongly bound  $N_2$

molecule is the predominant reservoir for nitrogen in both plasmas. Similarly to  $\{\text{NH}(\nu = 0)\}$ , the  $\text{NH}^*$  emission intensity exhibits an approximate power-law relationship to  $X_0(\text{N})$ , again with a smaller exponent ( $a = 0.47$ ) for the  $\text{NH}_3/\text{H}_2$  mixture than for  $\text{N}_2/\text{H}_2$  ( $a = 0.81$ ).

The  $\text{N}_2^*$  and  $\text{NH}^*$  emissions from  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  plasmas respond similarly to changes in applied microwave power as do  $\{\text{H}(n = 2)\}$  and  $\{\text{NH}(\nu = 0)\}$ , as may be seen by comparing the relevant data in Figures 8a and 5a. One notable



**Figure 8.**  $\text{NH}^*$  and  $\text{N}_2^*$  emission intensities measured (a) at  $z = 7$  mm ( $\text{N}_2/\text{H}_2$  plasma, 3/500 sccm, filled symbols) and  $z = 5$  mm ( $\text{NH}_3/\text{H}_2$  plasma, 6/500 sccm, open symbols) as a function of  $P$  and (b) at  $z = 5$  mm for  $\text{N}_2/\text{H}_2$  (3/500 sccm) and  $\text{NH}_3/\text{H}_2$  (6/500 sccm) plasmas (filled and open symbols, respectively) as a function of  $p$ . All other parameters were maintained at their base values, and the emission intensities for each species are mutually normalized to the maximal value measured at any  $P$ , in panel (a), or  $p$ , in panel (b), from either plasma. Calculated values of the (relative)  $\text{N}_2(\text{C} \leftarrow \text{X})$  and  $\text{NH}(\text{A} \leftarrow \text{X})$  EI excitation rates are shown as pale blue triangles and gray squares, respectively.

observation is that the  $\text{N}_2^*$  emission intensity increases less steeply with  $P$  than does  $\{\text{H}(n = 2)\}$ , despite the  $\text{H}(n = 2)$  energy (with respect to ground state H) being a little below that of  $\text{N}_2(\text{C}^3\Pi_u)$  with respect to its ground state, i.e., 10.2 and 11.0 eV, respectively. Further discussion and interpretation of these various observations draws on companion modeling studies of the plasma chemistry and composition which are described below.

#### 4. N/H PLASMA MODELING

Our description of the N/H plasma modeling starts by highlighting similarities (with regard to both processes and effects) associated with adding small amounts of  $\text{N}_2$  or  $\text{NH}_3$  (up to a few percent) to a  $\text{H}_2$  plasma. For both N source gases,

the 2-D model (elaborated below) shows  $\text{N}_2$  molecules to be the dominant N-containing species, representing  $\approx 99.99\%$  ( $\text{N}_2/\text{H}_2$ ) and  $\approx 92\%$  ( $\text{NH}_3/\text{H}_2$ ) of the total nitrogen content in the reactor under “base” conditions of power  $P = 1.5$  kW, pressure  $p = 150$  Torr, and input mole fraction  $X_0(\text{N}_2 \text{ or } \text{NH}_3) = 1.2\%$ . The N/H plasma-chemical kinetics and species concentrations in the hot plasma region thus share many common features. However, it is important to recognize a significant difference in the case of the  $\text{NH}_3/\text{H}_2$  gas mixture: the additional source of  $\text{NH}_x$  ( $x = 0-2$ ) species resulting from  $\text{NH}_3$  diffusion from the peripheral, cold regions of the reactor (primarily near the gas inlets) into the central hot plasma region.

Addition of either N-containing gas leads to a similar change in the dominant ions, from  $\text{H}_3^+$  in the case of the pure  $\text{H}_2$  plasma, to a mix of  $\text{NH}_4^+$  and  $\text{N}_2\text{H}^+$  ions in a N/H plasma operating at base conditions. With 1.2% addition of either  $\text{N}_2$  or  $\text{NH}_3$  precursor,  $[\text{H}_3^+]$  is reduced to less than 0.3% of  $([\text{NH}_4^+] + [\text{N}_2\text{H}^+])$ . We note, however, that the “pure”  $\text{H}_2$  plasmas used in the present experiments for measurements with no deliberately added N-containing gas will still contain trace amounts of air (i.e.,  $\text{N}_2$  and  $\text{O}_2$ ). Assuming, as in our previous studies of MW-activated B/H plasmas,<sup>31</sup> a worst-case scenario of 50 ppm air impurity (containing 40 ppm of  $\text{N}_2$  and 10 ppm of  $\text{O}_2$ ),  $\text{H}_3^+$  would already have been supplanted as the dominant ion by a mixture of  $\text{H}_3\text{O}^+$ ,  $\text{N}_2\text{H}^+$ , and  $\text{NH}_4^+$  ions with total concentration  $\approx 10^{11} \text{ cm}^{-3}$  and associated ion–electron recombination coefficients  $\beta \approx (0.5-2) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ . In practice, therefore, the ionization–recombination balance associated with the charged particles and the resulting plasma parameters (electron temperature  $T_e$  and density  $n_e$ ) will be perturbed little by small additions of  $\text{N}_2$  or  $\text{NH}_3$ . This expectation is consistent with the small increase in  $\text{H}_\alpha$  emission (Figure 7) and the lack of any discernible jump in the  $\text{H}_\alpha$  absorption measurements (Figure 4), and stands in marked contrast to the previously reported >100% increase in  $\text{H}_\alpha$  emission and  $\{\text{H}(n = 2)\}$  when adding  $\text{C}_x\text{H}_y$  to a  $\text{H}_2$  plasma.<sup>10,16,19</sup> In the case of an  $\text{N}_2/\text{H}_2$  plasma,  $\text{N}_2\text{H}^+$  is progressively supplanted as a major ion by  $\text{NH}_4^+$  upon increasing  $F(\text{N}_2)$  as a result of the reaction  $\text{N}_2\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{N}_2$ .

The N/H thermochemistry and plasma-chemical mechanism used in the present study were developed on the basis of GRI-Mech 3.0 for H,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_x$  ( $x = 0-3$ ),<sup>32</sup> expanded to involve (i)  $\text{N}_2\text{H}_x$  ( $x = 1-4$ ) species<sup>33,34</sup> and (ii) plasma chemistry for charged species and excited states involved in various ion conversion and electron–ion recombination reactions.<sup>35,36</sup> Also considered were species ionization, excitation of rovibrational states  $\text{H}_2(\nu, J)$ , and electron impact (EI) excitations forming  $\text{H}(n = 2, 3)$ , an “effective” excited state of molecular hydrogen with  $E_i > 11$  eV ( $\text{H}_2^*$ ), and  $\text{N}_2^*$ . As before,<sup>10</sup> rate coefficients for processes within block (ii) and their dependence on the local electron energy distribution function (EEDF) and reduced electric field ( $E/N$ , where  $N$  is the total number density) were estimated using a 0-D framework, wherein the kinetic equations for the EEDF and the local balance equations describing the plasma-chemical kinetics for the charged and neutral species were solved consistently for the range of  $E/N$  and  $T$  values of interest. Extensive chemical database analysis and test 2-D model calculations assuming various chemical schemes for the additional blocks (i) and (ii) result in the core N/H reaction mechanism presented in Table 1 (where some reactions found

Table 1. N/H Chemical Mechanism Used in the Present Study with the  $T$ - and  $T_c$ -Dependent Rate Coefficients  $k$  ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ )<sup>a</sup>

reaction	rate coefficient $k = AT^b \exp(-E/RT)$			$R_{\text{forward}}/(\text{cm}^3 \text{s})$	$R_{\text{reverse}}/(\text{cm}^3 \text{s})$
	$A$	$b$	$E$		
$\text{H} + \text{H} + \text{H}_2 \rightleftharpoons \text{H}_2 + \text{H}_2$	$9.00 \times 10^{16}$	-0.6	0	$1.179 \times 10^{18}$	$1.354 \times 10^{19}$
$\text{H} + \text{H} + \text{H} \rightleftharpoons \text{H}_2 + \text{H}$	$1.00 \times 10^{18}$	-1	0	$4.042 \times 10^{16}$	$4.641 \times 10^{17}$
$\text{NH}_3 + \text{H} \rightleftharpoons \text{NH}_2 + \text{H}_2$	$5.40 \times 10^5$	2.4	9915	$1.409 \times 10^{18}$	$1.410 \times 10^{18}$
$\text{NH}_2 + \text{H} \rightleftharpoons \text{NH} + \text{H}_2$	$4.00 \times 10^{13}$	0	3650	$4.379 \times 10^{17}$	$4.390 \times 10^{17}$
$\text{NH} + \text{H} \rightleftharpoons \text{N} + \text{H}_2$	$1.88 \times 10^8$	1.55	205	$7.205 \times 10^{17}$	$7.206 \times 10^{17}$
$\text{N} + \text{NH} \rightleftharpoons \text{N}_2 + \text{H}$	$3.00 \times 10^{13}$	0	0	$5.094 \times 10^{12}$	$5.655 \times 10^{11}$
$\text{N} + \text{NH}_2 \rightleftharpoons \text{N}_2 + \text{H} + \text{H}$	$7.26 \times 10^{13}$	0	0	$1.481 \times 10^{13}$	$1.436 \times 10^{11}$
$\text{N} + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H} + \text{H}$	$1.00 \times 10^{13}$	0	0	$2.039 \times 10^{12}$	$2.277 \times 10^{11}$
$\text{NH} + \text{NH} \rightleftharpoons \text{N}_2 + \text{H} + \text{H}$	$5.10 \times 10^{13}$	0	0	$7.523 \times 10^{12}$	$7.277 \times 10^{10}$
$\text{NH} + \text{NH} \rightleftharpoons \text{N}_2\text{H} + \text{H}$	$8.00 \times 10^{11}$	0.5	1987	$4.478 \times 10^{12}$	$4.989 \times 10^{11}$
$\text{NH} + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_2 + \text{H}$	$4.27 \times 10^{14}$	-0.272	-77	$8.784 \times 10^{12}$	$3.406 \times 10^{12}$
$\text{NH}_2 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_2 + \text{H}_2$	$1.70 \times 10^8$	1.62	11783	$1.861 \times 10^{12}$	$7.234 \times 10^{11}$
$\text{NH}_2 + \text{NH}_3 \rightleftharpoons \text{N}_2\text{H}_4 + \text{H}$	19	3.11	50115	$1.303 \times 10^8$	$3.458 \times 10^7$
$\text{N}_2\text{H}_4 + \text{H} \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$	$4.54 \times 10^7$	1.8	2613	$6.459 \times 10^8$	$9.143 \times 10^8$
$\text{N}_2\text{H}_3 + \text{H} \rightleftharpoons \text{N}_2\text{H}_2 + \text{H}_2$	$2.40 \times 10^8$	1.5	-10	$8.725 \times 10^9$	$9.042 \times 10^9$
$\text{N}_2\text{H}_2 + \text{H} \rightleftharpoons \text{N}_2\text{H} + \text{H}_2$	$3.60 \times 10^8$	1.58	1717	$8.158 \times 10^{12}$	$2.350 \times 10^{12}$
$\text{N}_2\text{H} + \text{H} \rightleftharpoons \text{N}_2 + \text{H}_2$	$3.60 \times 10^8$	1.58	1717	$3.673 \times 10^{15}$	$3.662 \times 10^{15}$
$\text{NH}_2 + \text{NH}_2 \rightleftharpoons \text{NH} + \text{NH}_3$	5.616	3.53	555	$1.770 \times 10^{12}$	$1.773 \times 10^{12}$
$\text{NH} + \text{M} \rightleftharpoons \text{N} + \text{H} + \text{M}$	$2.65 \times 10^{14}$	0	75 500	$1.156 \times 10^{14}$	$1.007 \times 10^{13}$
$\text{NH}_2 + \text{M} \rightleftharpoons \text{NH} + \text{H} + \text{M}$	$3.16 \times 10^{23}$	-2	91 400	$1.241 \times 10^{15}$	$1.084 \times 10^{14}$
$\text{NH}_3 + \text{M} \rightleftharpoons \text{NH}_2 + \text{H} + \text{M}$	$2.20 \times 10^{16}$	0	93 468	$1.770 \times 10^{15}$	$1.544 \times 10^{14}$
$\text{N}_2\text{H}_2 + \text{M} \rightleftharpoons \text{N}_2\text{H} + \text{H} + \text{M}$	$1.90 \times 10^{27}$	-3.5	66 107	$7.238 \times 10^{11}$	$1.816 \times 10^{10}$
$\text{NH} + \text{N} \rightleftharpoons \text{N}_2(\text{A3}) + \text{H}$	$4.50 \times 10^{10}$	0	0	$7.641 \times 10^9$	$1.233 \times 10^{14}$
$\text{N}_2(\text{A3}) + \text{H} \rightleftharpoons \text{N}_2 + \text{H}$	$1.26 \times 10^{14}$	0	0	$2.538 \times 10^{16}$	$1.746 \times 10^{11}$
$\text{N}_2(\text{A3}) + \text{H}_2 \rightleftharpoons \text{N}_2 + \text{H} + \text{H}$	$5.00 \times 10^{12}$	0	4450	$6.203 \times 10^{15}$	$3.717 \times 10^9$
$\text{N}_2(\text{A3}) + \text{NH}_3 \rightleftharpoons \text{NH}_2 + \text{H} + \text{N}_2$	$7.47 \times 10^{13}$	0	0	$5.475 \times 10^{11}$	$3.284 \times 10^5$
$\text{N} + \text{N} + \text{H}_2 \rightleftharpoons \text{N}_2(\text{A3}) + \text{H}_2$	$5.00 \times 10^{13}$	0	-997	$9.008 \times 10^6$	$1.669 \times 10^{12}$
$\text{N} + \text{N} + \text{N}_2 \rightleftharpoons \text{N}_2(\text{A3}) + \text{N}_2$	$3.00 \times 10^{14}$	0	-997	$1.701 \times 10^5$	$3.152 \times 10^{10}$
$\text{H}(n=3) \rightarrow \text{H}(n=2) + h\nu$	$4.40 \times 10^7$	0	0	$2.766 \times 10^{14}$	
$\text{H}(n=2) \rightarrow \text{H} + h\nu$	$4.70 \times 10^8$	0	0	$2.956 \times 10^{16}$	
$\text{H}(n=3) \rightarrow \text{H} + h\nu$	$5.50 \times 10^7$	0	0	$3.457 \times 10^{14}$	
$\text{H}_2^* \rightarrow \text{H}_2 + h\nu$	$2.00 \times 10^7$	0	0	$3.317 \times 10^{16}$	
$\text{H}_2(v=1) + \text{H} \rightarrow \text{H}_2(v=0) + \text{H}$	$1.26 \times 10^9$	1.35	2200	$1.210 \times 10^{23}$	
$\text{H}_2(v=0) + \text{H} \rightarrow \text{H}_2(v=1) + \text{H}$	$1.26 \times 10^9$	1.35	14 089	$1.208 \times 10^{23}$	
$\text{H}_2(v=1) + \text{H}_2 \rightarrow \text{H}_2(v=0) + \text{H}_2$	$1.88 \times 10^7$	1.5	9550	$2.213 \times 10^{22}$	
$\text{H}_2(v=0) + \text{H}_2 \rightarrow \text{H}_2(v=1) + \text{H}_2$	$1.88 \times 10^7$	1.5	21 439	$2.210 \times 10^{22}$	
$\text{H}(n=2) + \text{H}_2 \rightarrow \text{H} + \text{H} + \text{H}$	$1.00 \times 10^{13}$	0	0	$4.872 \times 10^{14}$	
$\text{H}(n=3) + \text{H}_2 \rightarrow \text{H} + \text{H} + \text{H}$	$1.00 \times 10^{13}$	0	0	$4.869 \times 10^{13}$	
$\text{H}(n=2) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{e}$	$1.00 \times 10^{13}$	0	16 130	$2.914 \times 10^{13}$	
$\text{H}(n=3) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{e}$	$1.00 \times 10^{13}$	0	0	$4.869 \times 10^{13}$	
$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$	$1.20 \times 10^{15}$	0	0	$3.242 \times 10^{14}$	
$\text{H}_2^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$	$1.20 \times 10^{15}$	0	0	$1.021 \times 10^{12}$	
$\text{H}_3^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}_2$	$1.08 \times 10^{15}$	0	0	$5.663 \times 10^{14}$	
$\text{H}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{H}_2$	$1.63 \times 10^{15}$	0	0	$7.330 \times 10^{11}$	
$\text{H}^+ + \text{H}_2 + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2$	$3.60 \times 10^{19}$	-0.5	0	$1.651 \times 10^{14}$	
$\text{N}_2^+ + \text{H}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$	$1.20 \times 10^{15}$	0	0	$1.303 \times 10^{12}$	
$\text{N}_2\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{N}_2$	$1.38 \times 10^{15}$	0	0	$3.081 \times 10^{14}$	
$\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$	$1.20 \times 10^{12}$	0	0	$3.560 \times 10^{11}$	
electron reactions	rate constant $k = AT_c^b \exp(-E/(RT_c))$			$R_{\text{forward}}/(\text{cm}^3 \text{s})$	$R_{\text{reverse}}/(\text{cm}^3 \text{s})$
	$A$	$b$	$E$		
$\text{H}(n=2) + \text{e} \rightarrow \text{H}(n=3) + \text{e}$	$2.53 \times 10^{16}$	0	43 775	$1.059 \times 10^{11}$	
$\text{H}(n=3) + \text{e} \rightarrow \text{H}(n=2) + \text{e}$	$3.10 \times 10^{16}$	0	0	$6.220 \times 10^{10}$	
$\text{H} + \text{e} \rightarrow \text{H}(n=2) + \text{e}$	$1.21 \times 10^{16}$	0	235 001	$2.980 \times 10^{16}$	
$\text{H}(n=2) + \text{e} \rightarrow \text{H} + \text{e}$	$1.17 \times 10^{16}$	0	0	$2.348 \times 10^{11}$	
$\text{H} + \text{e} \rightarrow \text{H}(n=3) + \text{e}$	$1.39 \times 10^{15}$	0	278 545	$7.197 \times 10^{14}$	
$\text{H}_2(v=0) + \text{e} \rightarrow \text{H}_2(v=1) + \text{e}$	$2.00 \times 10^{15}$	0	11 980	$1.725 \times 10^{20}$	
$\text{H}_2(v=1) + \text{e} \rightarrow \text{H}_2(v=0) + \text{e}$	$2.30 \times 10^{15}$	0	0	$3.826 \times 10^{19}$	
$\text{H}_2 + \text{e} \rightarrow \text{H} + \text{H} + \text{e}$	$2.43 \times 10^{15}$	0	191 226	$3.841 \times 10^{17}$	



Table 1. continued

electron reactions	rate constant $k = AT_e^b \exp(-E/(RT_e))$			
	A	b	E	
$H_2 + e \rightarrow H + H + e$	$8.88 \times 10^{15}$	0	267 260	$9.203 \times 10^{16}$
$H_2 + e \rightarrow H_2^* + e$	$3.20 \times 10^{15}$	0	267 260	$3.317 \times 10^{16}$
$H_2^* + e \rightarrow H_2 + e$	$1.00 \times 10^{15}$	0	0	$5.302 \times 10^{11}$
$N_2 + e \rightarrow N + N + e$	$5.12 \times 10^{14}$	0	282 231	$9.772 \times 10^{12}$
$N_2 + e \rightarrow N + N + e$	$1.87 \times 10^{15}$	0	287 991	$2.900 \times 10^{13}$
$NH_3 + e \rightarrow NH_2 + H + e$	$1.20 \times 10^{16}$	0	184 000	$6.667 \times 10^{12}$
$NH_2 + e \rightarrow NH + H + e$	$1.20 \times 10^{16}$	0	184 000	$1.884 \times 10^{12}$
$N_2 + e \rightarrow N_2(A3) + e$	$1.10 \times 10^{16}$	0	142 153	$3.171 \times 10^{16}$
$H_2^* + e \rightarrow H_2^+ + e + e$	$4.84 \times 10^{15}$	0	88 241	$1.087 \times 10^{11}$
$H + e \rightarrow H^+ + e + e$	$1.11 \times 10^{15}$	0	313 330	$1.651 \times 10^{14}$
$H_2 + e \rightarrow H_2^+ + e + e$	$7.23 \times 10^{14}$	0	354 810	$3.251 \times 10^{14}$
$N_2 + e \rightarrow N_2^+ + e + e$	$1.09 \times 10^{15}$	0	359 413	$1.303 \times 10^{12}$
$NH_3 + e \rightarrow NH_3^+ + e + e$	$6.81 \times 10^{15}$	0	249 976	$3.560 \times 10^{11}$
$H_2^+ + e \rightarrow H(n=2) + H$	$5.00 \times 10^{18}$	−0.67	0	$9.277 \times 10^8$
$H_3^+ + e \rightarrow H_2 + H(n=2)$	$2.89 \times 10^{14}$	0	0	$1.980 \times 10^{10}$
$N_2H^+ + e \rightarrow N_2 + H$	$2.50 \times 10^{19}$	−0.9	0	$1.569 \times 10^{14}$
$NH_4^+ + e \rightarrow NH_3 + H$	$3.00 \times 10^{18}$	−0.67	0	$1.375 \times 10^{14}$
$NH_4^+ + e \rightarrow NH_2 + H + H$	$3.00 \times 10^{18}$	−0.67	0	$1.375 \times 10^{14}$

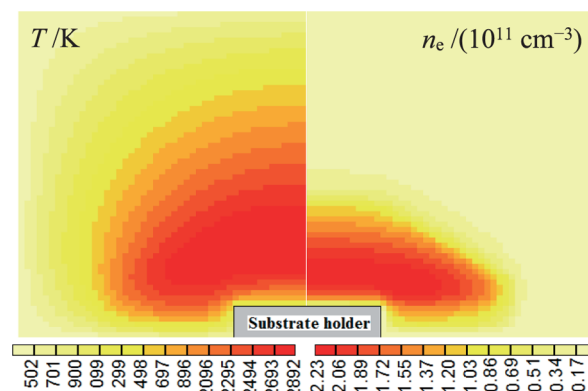
<sup>a</sup> $N_2(A3)$  represents the metastable  $A^3\Sigma_u^+$  state (the lowest energy triplet state) of  $N_2$ . The last two columns show the forward and reverse reaction rates calculated in the core (i.e.,  $r = 0$ ,  $z = 10.5$  mm) of a 1.2%  $N_2/H_2$  plasma with  $T = 2882$  K and  $T_e = 1.21$  eV (14 042 K), for  $P = 1.5$  kW and  $p = 150$  Torr. Units: cal, cm, s, K,  $R = 1.987\,262$  cal (mol K)<sup>−1</sup>, M is a third body, and the gas temperature  $T$  and electron temperature  $T_e$  are quoted in K.

to be unimportant under any conditions relevant to the present work have been omitted for brevity).

As in our previous analyses of activated C/H and N/H gas mixtures,<sup>10,18</sup> fast H-shifting reactions establish the concentration distributions of  $N_1H_x$  ( $x = 0-3$ ) and  $N_2H_x$  ( $x = 0-4$ ) species. However, these are sensitive not only to the local gas temperature and  $[H]/[H_2]$  ratio, but also to transport processes (diffusion, thermodiffusion, and flow transfer) and gas–surface reactions at the substrate, the substrate holder, the quartz window, and the reactor walls. The less stable  $N_2H_x$  ( $x = 1-4$ ) species survive only in the cold, near-wall regions. The most problematic parts of the mechanism are the less-well-established exchange processes between the  $N_1H_x$  and  $N_2H_x$  families, which could involve contributions from both heterogeneous reactions and reactions involving excited species (e.g.,  $N_2^*$ ), as discussed below.

**4.1.  $N_2/H_2$  and  $NH_3/H_2$  Plasma Activation and Dependences on  $X_0(N)$ .** **4.1.1.  $N_2/H_2$  Mixtures.** The present analysis of the N/H chemistry in MWCVD reactors starts with the simpler  $N_2/H_2$  gas mixtures, wherein nitrogen species conversion begins with dissociation of  $N_2$ . The ground state  $N_2(X^1\Sigma_g^+)$  molecule, henceforth identified as simply  $N_2$ , has a high bond strength:  $D_0(N\equiv N) = 9.78$  eV. Thus, the first issue to address is the dominant  $N_2$  dissociation mechanism under typical plasma conditions of  $T_e \approx 1.1-1.3$  eV and  $(r, z)$  distributions of gas temperature  $T$  and electron density  $n_e$  as in Figure 9. The obvious inhomogeneity of these distributions serves to illustrate some of the challenges to reproducing and interpreting experimental CRDS and OES data.

Two-dimensional model runs with the available N/H chemistry rule out a purely thermal mechanism given prevailing gas temperatures  $T < 3000$  K: reactions involving ground state neutral species (e.g.,  $N_2 + H \rightarrow NH + N$ ) simply do not provide sufficient activation, and calculations on this basis return NH column densities that are orders of magnitude lower than the measured  $\{NH(\nu = 0)\}$  as given in Figures 3 and 4.



**Figure 9.** Two-dimensional  $(r, z)$  distributions of gas temperature  $T$  and electron concentration  $n_e$  for base conditions and 1.2%  $N_2/H_2$  mixture. The model assumes cylindrical symmetry, a substrate diameter of 3 cm, and a reactor radius,  $R_r = 6$  cm, and height,  $h = 6.2$  cm.

We note that previously proposed wall reactions<sup>14,15</sup> are also unable to provide NH densities comparable to those observed. Given the calculated EEDF, we estimate a rate coefficient,  $k_{1,diss} < 5 \times 10^{-13}$  cm<sup>3</sup> s<sup>−1</sup>, for  $N_2$  dissociation by EI:



Reaction 1 is thus a relatively more important  $N_2$  dissociation route, but still fails (by an order of magnitude) to support the measured NH column densities. Other suggested dissociation mechanisms in  $N_2$  plasmas, involving electronically excited  $N_2^*$  and vibrationally excited  $N_2(\nu \geq 14)$  molecules,<sup>37</sup> are also unimportant in the present case.

Seeking other possible  $N_2$  dissociation mechanisms, we considered excited states of  $N_2$ , and particularly its lowest, metastable  $A^3\Sigma_u^+$  state, henceforth denoted as  $N_2(A3)$ . This has an excitation threshold  $\varepsilon = 6.2$  eV, and higher triplet states, including the C and B states involved in the  $N_2^*$  OES

spectrum, can also decay (radiatively and/or collisionally) to  $N_2(A3)$ . Thus,  $N_2(A3)$  has been included in the kinetic scheme (Table 1) and an excitation rate coefficient  $k_2$  for the process



calculated from the EEDF, with additional contributions to account for cascades from higher triplet states of  $N_2$ . Typical values of  $k_2$  for the present MW plasma conditions are  $k_2[\text{cm}^3 \text{s}^{-1}] = 1.8 \times 10^{-8} \times \exp(-6.2/T_e[\text{eV}])$ . From the perspective of dissociating  $N_2$ , the most effective way to use this electronic excitation appears to be through the spin-allowed reaction 3 with H atoms, which is the most populous radical in the present study, with typical mole fractions  $X(\text{H}) \approx 5\text{--}10\%$  in the plasma core. That is



with rate coefficient  $k_3$  yet to be determined. One fast discharge flow study<sup>38</sup> concluded that reaction 3 is improbable, but careful inspection of that data allows an alternative interpretation that is compatible with the kinetics proposed here. The prior conclusion was based on an observation that H atom addition to a  $N_2(A3)/H_2$  mixture caused no discernible increase in measured NH. Our simulations of the earlier experimental conditions suggest that the NH concentration would actually increase at early reaction times by reaction 3, but then decline (due to the reaction  $\text{NH} + \text{H} \rightarrow \text{N} + \text{H}_2$ ) in contrast to the steady growth in  $[\text{NH}]$  observed in experiments with no added H atoms. Assuming  $k_3 < 2.8 \times 10^{-15} \text{ cm}^3 \text{s}^{-1}$  at  $T = 295 \text{ K}$  (the temperature of the fast discharge flow experiment), the predicted NH concentration at the time of measurement,  $t = 14 \text{ ms}$ , is indeed lower than with no added H atoms, which is consistent with the prior observation. More detailed discussion and reinterpretation of the earlier experimental results is reserved for the Appendix.

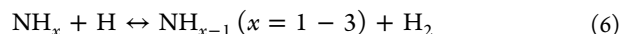
The proposed source of  $\text{NH}_x$  through reaction 3 will, however, be reduced by competition with the fast deactivation of  $N_2(A3)$  through collision with H and  $H_2$ :



The evaluation by Herron<sup>39</sup> recommends rate coefficients  $k_4 = 2.1 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$  and  $k_5(298 \text{ K}) \approx (4 \pm 2) \times 10^{-15} \text{ cm}^3 \text{s}^{-1}$ , while Slanger et al.<sup>40</sup> have  $k_5(T) = 2.2 \times 10^{-10} \exp(-3500/T)$  over the limited temperature range  $240 < T < 370 \text{ K}$ . The present MWCVD model requires  $k_5(T)$ , as well as  $k_3(T)$ , over the much wider temperature range  $300 < T < 3000 \text{ K}$ . Given typical values of  $X_{\text{H}} \approx 5\text{--}10\%$  in the plasma region, reaction 4 will be the dominant quenching reaction provided that  $k_5$  shows only a limited increase with  $T$ , i.e., if  $k_5 < 5 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$  at  $T = 3000 \text{ K}$ . For determinacy, we have assumed this condition and hence set  $k_5(T) = 8.3 \times 10^{-12} \exp(-2239/T)$ , which reproduces both the Slanger et al. measurements<sup>40</sup> at  $T = 370 \text{ K}$  and Herron's recommended value<sup>39</sup> of  $k_5(298 \text{ K})$ . A consequence of this assumption, however, is that the  $k_3(T)$  values that we now deduce for the plasma core region (at  $T \approx 2500\text{--}3000 \text{ K}$ ) should be regarded as lower bounds. Proceeding as such, we note that the rate coefficient for  $\text{NH} + \text{N} \rightarrow N_2 + \text{H}$  is temperature-independent ( $k = 5 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$ , cf., Table 1), and have taken  $k_{-3}$  to be similarly independent of temperature. Combining an assumed value of  $k_{-3} = 7.5 \times 10^{-14} \text{ cm}^3 \text{s}^{-1}$  with known thermochemical data gives the rate coefficient  $k_3(T) [\text{cm}^3 \text{s}^{-1}] \approx 2 \times 10^{-12}$

$\exp(-1937/T)$ , which is able both to reproduce the  $\{\text{NH}(v = 0)\}$  values measured in the present  $N_2/H_2$  MW plasma and to reinterpret the fast discharge flow data<sup>38</sup> with  $k_3(295 \text{ K}) = 2.8 \times 10^{-15} \text{ cm}^3 \text{s}^{-1}$ .

Having resolved the issue of the primary sources of N and NH species, we are now able to describe further interconversions between the N-containing species. N and NH formed in the plasma region, mainly via reaction 3, participate in fast H-shifting reactions

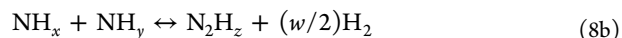
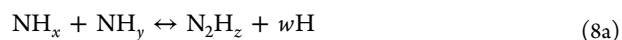


resulting in populations of  $\text{NH}_2$  and  $\text{NH}_3$ . The family of reactions 6, with rates that depend on the local  $[\text{H}]$ ,  $[\text{H}_2]$  and gas temperature  $T(r, z)$ , along with  $\text{NH}_x$  transport mainly by diffusional and thermodiffusional transfer between hot and cold regions, determine the complex equilibrium between the various  $\text{NH}_x$  species throughout the entire reactor.

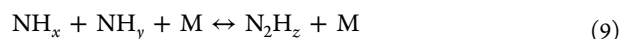
In addition, the global balance of N-containing species is determined by the input flow  $F(N_2)$  and outflow from the reactor (wherein  $[\text{N}_2]$  is still very much greater than the sum of the concentrations of all other N-containing species, including  $\text{NH}_3$ ), and the slow interconversion between  $\text{NH}_x$  and  $\text{N}_2\text{H}_x$  species. As discussed above,  $\text{N}_2\text{H}_x \rightarrow 2\text{NH}_y$  conversion is mainly via reaction 3 and, to a lesser extent, reaction 1. The reverse conversion is determined by the reaction



with additional contributions from many (generally poorly determined) two-body recombination reactions



where  $w = (x + y) - z$ , as well as the analogous three-body recombinations



Among these, the reactions  $\text{N} + \text{NH}_2 \leftrightarrow \text{N}_2 + 2\text{H}$  and  $2\text{NH} \leftrightarrow \text{N}_2 + 2\text{H}$  are the most important under the conditions of the present study. Heterogeneous recombination reactions of  $\text{NH}_x$  species at the metal reactor walls and/or the hot quartz window are also possible, but seemingly unimportant for  $N_2/H_2$  mixtures. This is, however, in marked contrast to the case with  $\text{NH}_3/H_2$  mixtures, as discussed below.

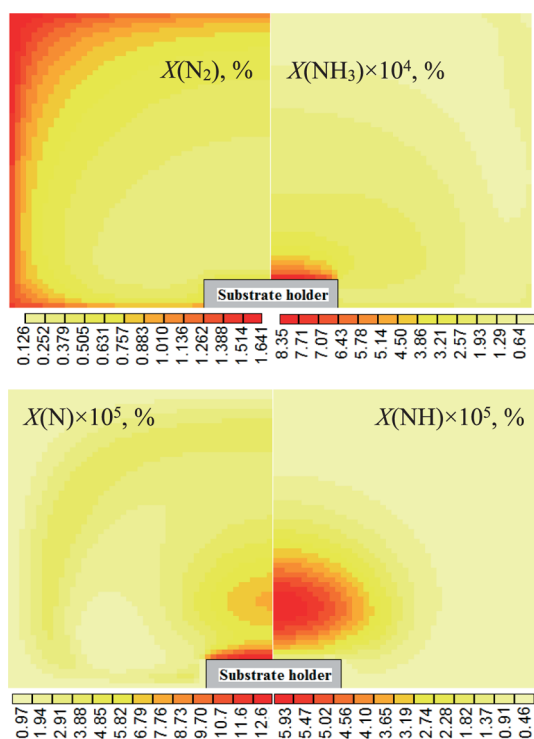
The above-mentioned processes have obvious parallels with those reported previously<sup>10,16</sup> for carbonaceous species in MW-activated C/H plasmas, wherein  $\text{C}_2\text{H}_2$  is the dominant C-containing species in the hot plasma region irrespective of the choice of carbon source gas, and  $\{\text{CH}\}$  was shown both experimentally and theoretically to scale as  $X_0(\text{C})^{0.5}$ , where  $X_0(\text{C})$  is the input carbon atom mole fraction. Here,  $\text{N}_2$  is the dominant N-containing species, and we can undertake a similar analysis of the production and loss rates for the  $\text{NH}_x$  species in the hot plasma region per reactions 1, 3, and 7–9. The resulting overall balance of  $\text{N}_1$  species can be written as

$$[\text{N}_1] \times b_{\text{diff,plasma}} + [\text{N}_1]^2 \times b_{\text{rec}} \approx n_e \times [\text{N}_2] \times b_{\text{diss,1}} + [\text{N}_2(A3)] \times [\text{H}] \times b_{\text{diss,3}} \quad (10)$$

where  $[\text{N}_1] = \sum[\text{NH}_x]$  ( $x = 0\text{--}3$ ), and the proportionality coefficients  $b$  are independent of  $X_0(\text{N})$  in the process gas. The terms on the left-hand side represent  $\text{N}_1$  loss processes, namely,

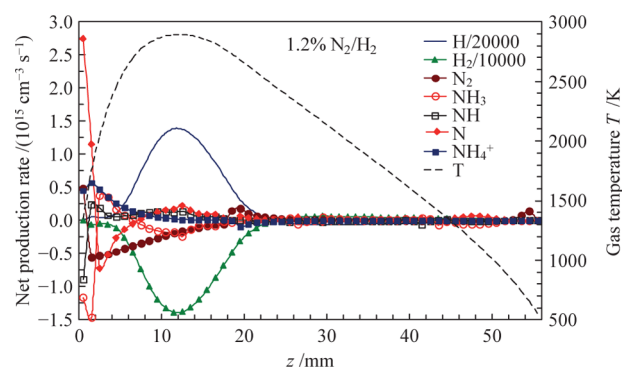
through diffusion out of the hot region of the plasma (with relative rate  $b_{\text{diff,plasma}}$ ) and reaction ( $b_{\text{reac}}$ ) according to any of reactions 7–9, while the terms on the right represent sources, i.e., the dissociation reactions 1 and 3, respectively. This illustrative balance can be used to obtain the functional dependence of  $\{\text{NH}_x\}$  on  $X_0(\text{N})$ , and for the NH radical, which is concentrated in the hot plasma core, eq 10 predicts  $\{\text{NH}\} \sim X_0(\text{N})^a$ . The exponent  $a$  may lie between 0.5, in the case that reactions 7–9 are the dominant NH loss processes, and 1.0, if  $\text{NH}_x$  loss is instead dominated by axial diffusion from the hot plasma core to colder regions near the quartz window and the reactor base plate. The 2-D model predicts a near-linear relationship between  $\{\text{NH}\}$  and  $X_0(\text{N})$ , implying that diffusion should dominate, whereas the CRDS and OES measurements are best described by intermediate exponents, as shown in Figure 4a, where  $a = 0.70$ , and Figure 7, which has  $a = 0.81$ .

The foregoing analysis identifies the hot plasma as the main source of  $\text{NH}_x$  ( $x = 0-3$ ) species in a MWCVD process employing a  $\text{N}_2/\text{H}_2$  gas mixture, and the spatial distributions of the  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{N}$ , and  $\text{NH}$  mole fractions returned by the 2-D model, shown in the form of  $(r, z)$  maps in Figure 10, are all



**Figure 10.** Two-dimensional  $(r, z)$  plots showing the mole fractions of  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{N}$ , and  $\text{NH}$  in a 1.2%  $\text{N}_2/\text{H}_2$  gas mixture with  $P = 1.5$  kW,  $p = 150$  Torr, and reactor dimensions as defined in the caption to Figure 9.

consistent with production of  $\text{N}_1$  species in the plasma core and their subsequent diffusion out to the cooler regions. (The spatial distribution of the  $\text{NH}_2$  mole fraction closely resembles that for  $\text{NH}$ , and is therefore not shown.)  $\text{N}_2$  molecules, in contrast, diffuse into the plasma region, where they decompose via reactions 1 and 3. Figure 11 shows net production rates for selected species, including  $\text{NH}_x$  ( $x = 0-3$ ), calculated at  $r = 0$  as a function of  $z$  (i.e., vertical distance above the center of the substrate). The local maxima and minima at  $z \approx 19$  mm are due to a boundary volume characterized by extensive recombination



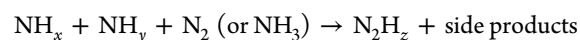
**Figure 11.** Net production (i.e., production–loss) rates of selected species plotted as a function of  $z$  in a 1.2%  $\text{N}_2/\text{H}_2$  gas mixture, for  $r = 0$ ,  $P = 1.5$  kW, and  $p = 150$  Torr.

of ions and electrons diffusing away from the plasma, but without any compensating ionization because of the declining electric field in this region. The  $\text{N}$  data illustrates much of the complex reactivity: the calculations reveal net production of  $\text{N}$  atoms in the hot plasma region ( $z \approx 12$  mm) through reactions 1 and 3, net loss at smaller  $z$  due to re-equilibration into the various  $\text{N}_1$  species, and net production again as  $z \rightarrow 0$ , reflecting the temperature dependence of both the equilibrium constants for the various H-shifting reactions 6 and the local  $[\text{H}]/[\text{H}_2]$  ratio. Numerical experiments confirm that the conversion and transport of N-containing species described in this section will be (at most) only weakly perturbed by surface-mediated heterogeneous reactions of  $\text{NH}_x$  species, in marked contrast to the case of MW activated  $\text{NH}_3/\text{H}_2$  mixtures, which we now consider.

**4.1.2.  $\text{NH}_3/\text{H}_2$  Mixtures.** Two-dimensional modeling of the MW-activated  $\text{NH}_3/\text{H}_2$  plasma following the same N/H gas-phase chemistry described above (Table 1) yields more extended  $\text{NH}_x$  spatial distributions (Figure 12), with the positions of maximal mole fraction for each species lying further from the plasma core and more toward the source gas inlets than in the  $\text{N}_2/\text{H}_2$  case (Figure 10). Furthermore, the predicted directions of diffusional flux are here species-specific due to the presence of an alternative, and dominant,  $\text{NH}_x$  source term: axial and radial diffusion of  $\text{NH}_3$  from the near-inlet region to all other parts of the reactor volume. Two terms dominate the  $\text{N}_1$  species balance within the measurement region ( $0 < z < 20$  mm), namely,  $\text{NH}_3$  diffusion from the gas inlet region and reactive loss:

$$[\text{N}_1]^2 \times b_{\text{reac}} \approx [\text{NH}_3] \times b_{\text{diff(inlet)}} \quad (11)$$

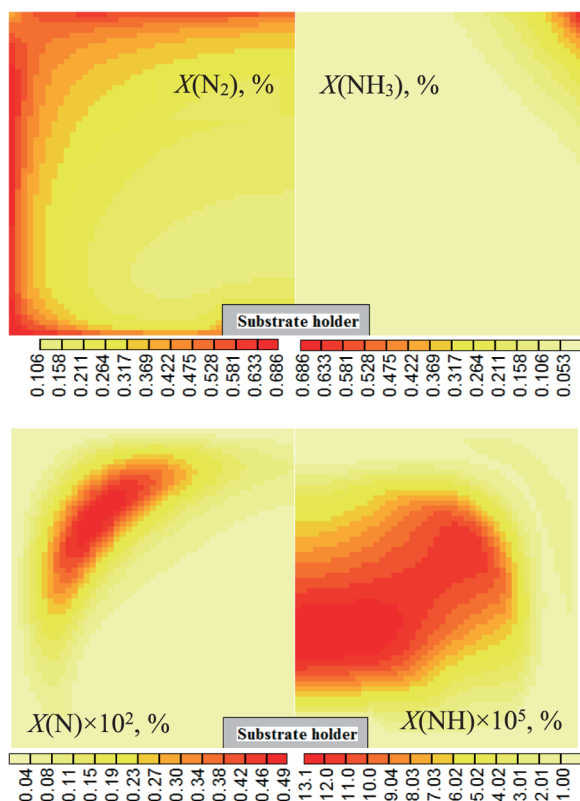
Equation 11 implies a square-root dependence, i.e.,  $\{\text{NH}\} \sim X_0(\text{N})^{0.5}$ , which is reproduced in both the 2-D model results and the OES measurements, with the latter being well-described by an exponent  $a = 0.47$ . Analysis of the CRDS measurements, however, returns  $a = 0.36$ . Such a (close to) cube-root dependence on  $X_0(\text{N})$  could be realized if  $\text{NH}_x$  loss was dominated by one or more three-body reactions, such as



but the present calculations suggest that any such reaction would need to have an improbably large rate coefficient ( $k > 10^{-28} \text{ cm}^6 \text{ s}^{-1}$ ) to be practically important.

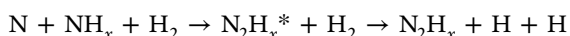
The global  $\text{N}_1$  balance for  $\text{NH}_3/\text{H}_2$  plasmas constitutes another, and more serious, discrepancy between the calculated and measured  $\{\text{NH}(\nu = 0)\}$   $z$ -profiles. The predicted  $\{\text{NH}\}$



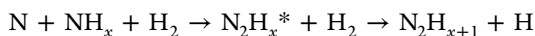


**Figure 12.** Two-dimensional ( $r, z$ ) plots showing the mole fractions of  $N_2$ ,  $NH_3$ ,  $N$ , and  $NH$  in a 1.2%  $NH_3/H_2$  gas mixture with  $P = 1.5$  kW,  $p = 150$  Torr, and reactor dimensions as defined in the caption to Figure 9.

values exceed the measured column densities by factors of 2–3 at  $z < 15$  mm, peaking at  $z \approx 35$  mm, far from the hot plasma core; however, the measured  $\{NH(\nu = 0)\}$  has maximized by  $z \approx 15$  mm. Various processes could lead to a reduction in the calculated  $[N_1]$  at large  $z$ : (i) Conversion of  $N_1$  species to  $N_2$ , by adsorption of  $NH_x$  ( $x = 0, 1$ ) at the reactor walls and on the hot quartz window, with subsequent gas–surface reactions with  $NH_3$  producing gas-phase  $N_2H_{4-x}$ , finally becoming  $N_2$  through a sequence of H-abstractions. Calculations show that such conversions will indeed reduce  $[N_1]$ , but not sufficiently to match the experimental observations given that  $[NH_3] > 10^{16}$   $cm^{-3}$  near the gas inlet far exceeds  $[N]$  and  $[NH]$ . Consequently, an adequate reduction of  $[N_1]$  would require  $NH_3$  loss at the surface with probability  $\gamma > 2 \times 10^{-4}$ , independent of the local N and NH fluxes. Such a large value of  $\gamma$  appears unphysical, however, on the basis of the critical sensitivity of the model results to the properties of the near-inlet region. (ii) Contributions from three-body reactions stabilized by collisions with  $H_2$ , e.g.



or

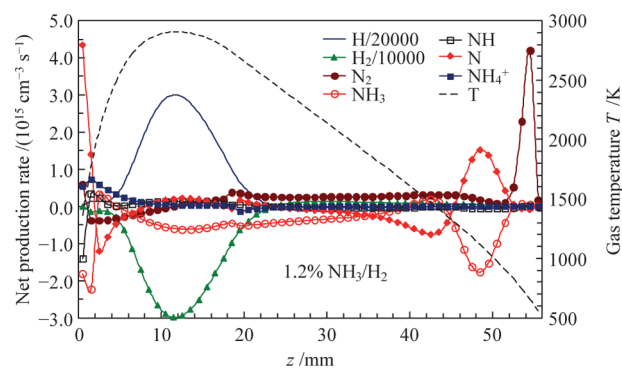


Such reactions cannot be important in practice, however, as they only give a useful reduction of  $[N_1]$  if we assume unrealistically large rate coefficients,  $k > 10^{-29}$   $cm^6 s^{-1}$ .

The most likely cause of this discrepancy, therefore, is the use of a cylindrically symmetric model geometry to describe the gas inlet scheme of the experimental PACVD reactor. Indeed, a

similar situation arose in our previous study of MW-activated  $CH_4/CO_2/H_2$  plasmas.<sup>17</sup> The process gas enters the reactor through two diametrically opposed ports positioned at  $\varphi \approx 45^\circ$  to the probe axis, whereas the 2-D ( $r, z$ ) model assumes gas entry at  $r = 60$  mm. As Figure 12 shows, the calculated  $NH_3$  mole fraction in a 1.2%  $NH_3/H_2$  plasma falls rapidly with increasing distance from the inlet, which suggests that, in the experiment, there are two sharply localized near-inlet regions where  $[NH_3] > 10^{16}$   $cm^{-3}$  and which extend  $< 10$  mm from the respective inlets. The combined volume of these two regions is far smaller than the cylindrically symmetric approximation of a cloud extending from an inlet ring  $2\pi r \approx 38$  cm in circumference. Acknowledging the sensitivity of the  $NH_x$  radical densities to the  $NH_3$  spatial distribution, we anticipate this difference between the experimental and modeled reactor geometries to be primarily responsible for the observed discrepancies. In contrast, in the  $N_2/H_2$  mixtures,  $N_2$  molecules are so stable and so dominant relative to all other N-containing species that they inevitably adopt a near cylindrically symmetric concentration distribution throughout the reactor volume, so that the calculated  $N_2$  distribution (Figure 10) deviates little from that of the experiment, regardless of inlet geometry.

A comparison of calculated ( $r, z$ ) maps of the  $N_2$ ,  $NH_3$ ,  $N$ , and  $NH$  mole fractions for an  $NH_3/H_2$  plasma (Figure 12) and the corresponding  $z$ -dependent net production rates at  $r = 0$  (Figure 13) with the corresponding plots for the  $N_2/H_2$  case



**Figure 13.** Net production (i.e., production–loss) rates of selected species plotted as a function of  $z$  in a 1.2%  $NH_3/H_2$  gas mixture, for  $r = 0$ ,  $P = 1.5$  kW, and  $p = 150$  Torr.

(Figures 10 and 11) highlights major differences, both in the regions in which the  $NH_x$  radicals are initially activated, and in the directions of their respective diffusional fluxes. The relatively weak bonding in  $NH_3$ , in contrast to that of  $N_2$ , is illustrated by the net loss of  $NH_3$  and production of  $N$  seen in Figure 13 at  $z \approx 50$  mm. In the region  $45 > z > 35$  mm,  $T$  increases, and the equilibria associated with the H-shifting reactions 6 shift in favor of  $NH_x$  ( $x > 0$ ). Further increasing  $T$  at  $35 > z > 25$  mm leads again to  $NH_3$  loss, the net rate of which reaches a local maximum, with corresponding  $N_2$  and  $N$  formation, in the warm recombinative region at  $z \approx 19$  mm. Below this lies the plasma proper, where the rising electron density and significant power absorption contribute to a maximum of  $T$ , and therefore of  $[H]$ . At still smaller  $z$ ,  $T$  falls and  $n_e$  further increases, leading to the loss of  $N$  and  $N_2$  and production of both  $NH_3$  and the major ions,  $N_2H^+$  and  $NH_4^+$ . Very close to the substrate,  $z < 3$  mm,  $NH_x$  ( $x > 0$ ) is consumed and  $N$  atoms are generated, with the latter constituting the dominant N-containing species in this region.



Overall, the present calculations succeed in rationalizing the basic conversions and balance within the N/H plasma-chemical kinetic scheme, and are able to account qualitatively (and, in many cases, quantitatively) for the experimental observations.

**Table 2. Calculated Concentrations (in  $\text{cm}^{-3}$ ) of Selected Species at Positions  $(r, z) = (0 \text{ mm}, 8.0 \text{ mm})$  and  $(0 \text{ mm}, 0.5 \text{ mm})$  in  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  Plasmas Operating under Base Conditions**

mixture	1.2% $\text{N}_2$ in $\text{H}_2$		1.2% $\text{NH}_3$ in $\text{H}_2$	
$z/\text{mm}$	8.0	0.5	8.0	0.5
$T/\text{K}$	2799	1354	2821	1364
$\text{H}_2$	$4.85 \times 10^{17}$	$1.06 \times 10^{18}$	$4.81 \times 10^{17}$	$1.05 \times 10^{18}$
$\text{N}_2$	$1.54 \times 10^{15}$	$5.51 \times 10^{15}$	$7.48 \times 10^{14}$	$2.68 \times 10^{15}$
$e$	$2.09 \times 10^{11}$	$6.76 \times 10^{10}$	$2.22 \times 10^{11}$	$7.52 \times 10^{10}$
$\text{H}(n=1)$	$3.09 \times 10^{16}$	$7.50 \times 10^{15}$	$3.19 \times 10^{16}$	$7.83 \times 10^{15}$
$\text{H}(n=2)$	$7.05 \times 10^7$	$1.97 \times 10^6$	$8.39 \times 10^7$	$2.49 \times 10^6$
$\text{H}(n=3)$	$7.21 \times 10^6$	$1.47 \times 10^5$	$8.72 \times 10^6$	$1.89 \times 10^5$
$\text{N}_2(\text{A}3)$	$4.79 \times 10^9$	$7.66 \times 10^9$	$2.53 \times 10^9$	$4.26 \times 10^9$
$\text{N}_2\text{H}$	$5.58 \times 10^8$	$1.94 \times 10^7$	$3.14 \times 10^8$	$4.22 \times 10^7$
$\text{N}_2\text{H}_2$	$2.03 \times 10^6$	$6.07 \times 10^6$	$5.46 \times 10^6$	$1.33 \times 10^7$
$\text{NH}_3$	$1.58 \times 10^{12}$	$8.94 \times 10^{12}$	$2.63 \times 10^{12}$	$1.28 \times 10^{13}$
$\text{NH}_2$	$3.75 \times 10^{11}$	$1.12 \times 10^{11}$	$6.53 \times 10^{11}$	$1.70 \times 10^{11}$
$\text{NH}$	$2.87 \times 10^{11}$	$1.11 \times 10^{11}$	$5.11 \times 10^{11}$	$1.71 \times 10^{11}$
$\text{N}$	$3.20 \times 10^{11}$	$1.35 \times 10^{12}$	$5.74 \times 10^{11}$	$2.04 \times 10^{12}$
$\text{H}_2^+$	$4.79 \times 10^5$	$3.33 \times 10^4$	$5.74 \times 10^5$	$4.24 \times 10^4$
$\text{H}_3^+$	$2.69 \times 10^8$	$8.36 \times 10^6$	$6.62 \times 10^8$	$2.34 \times 10^7$
$\text{N}_2\text{H}^+$	$1.13 \times 10^{11}$	$2.46 \times 10^{10}$	$9.32 \times 10^{10}$	$2.06 \times 10^{10}$
$\text{NH}_4^+$	$9.52 \times 10^{10}$	$4.30 \times 10^{10}$	$1.28 \times 10^{11}$	$5.45 \times 10^{10}$

Table 2 summarizes the calculated concentrations of selected species at the approximate center of the plasma,  $(r, z) = (0 \text{ mm}, 8.0 \text{ mm})$ , and immediately above the substrate, at  $(0 \text{ mm}, 0.5 \text{ mm})$ , for both  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  mixtures under base conditions. The calculated concentrations of the various  $\text{NH}_x$  ( $0 \leq x \leq 2$ ) species are similar in the hot plasma core, but among this family, N is predicted to be dominant close to the substrate. The calculations also predict only modest (less than a factor of 2) differences in these species concentrations in the  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  plasmas. We note, however, that  $X_0(\text{N})$  in the modeled  $\text{NH}_3/\text{H}_2$  plasma is only half that used in the  $\text{N}_2/\text{H}_2$  plasma modeling.

**4.2. Variations with Applied MW Power and Total Gas Pressure.** The calculated EEDF is primarily determined by the reduced electric field ( $E/N$ ), and does not vary with pressure  $p$  at constant  $E/N$ .<sup>10</sup> Here, we use the previously derived functional form of the absorbed power density, eq 12, to understand the possible changes in plasma parameters and the plasma volume  $V_{\text{pl}}$ , with changes in  $p$ .<sup>10,36</sup> That is

$$Q \sim C \times (E/N)^2 \times (p/T) \times (n_e/10^{11}) \quad (12)$$

where the input power  $P = \int Q \cdot dV_{\text{pl}}$ . Here, the power density  $Q$  has units of  $\text{W cm}^{-3}$ ,  $E/N$  is in Townsend units ( $1 \text{ Td} = 10^{-17} \text{ V cm}^2$ ),  $p$  is in Torr, and  $n_e$  is in  $\text{cm}^{-3}$ . The coefficient  $C \approx 0.25$  is essentially constant for the present  $\text{H}_2$ -rich plasmas.

**4.2.1. Power Dependences.** Two-dimensional model calculations for the 1.2%  $\text{N}_2/\text{H}_2$  mixture under base conditions and  $P = 0.8 \text{ kW}$  suggest that the measured changes upon increasing  $P$  from 0.8 to 1.5 kW are largely explicable by taking  $V_{\text{pl}} \sim P$ , per eq 12, while  $n_e \approx 2.2 \times 10^{11} \text{ cm}^{-3}$  and  $T_e \approx 1.24 \text{ eV}$  at the plasma center both remain essentially constant. The calculated maximum gas temperature,  $T_{\text{max}}$ , increases by  $\approx 4\%$ ,

from 2770 to 2890 K, as a result of this increase in  $P$ . These increases in  $T_{\text{max}}$  and  $V_{\text{pl}}$  are predicted to cause a 3-fold increase in total  $[\text{H}]$  within the entire reactor volume and a more than 2-fold increase in maximal  $[\text{H}]$ , in good accord with the observed increases in  $\{\text{H}(n=2)\}$  when using both dilute  $\text{N}_2/\text{H}_2$  and  $\text{NH}_3/\text{H}_2$  source gas mixtures (as shown in Figure 5a).

This increase in  $[\text{H}]$  elicits a more than 4-fold increase in the calculated  $\{\text{NH}(\nu=0)\}$ , consistent with the measured increases in both  $\{\text{NH}(\nu=0)\}$  and the  $\text{NH}^*$  emission intensities from the  $\text{N}_2/\text{H}_2$  plasma, as shown in Figures 5a and 8a. The  $\text{N}_2$  concentration is barely affected by these changes in  $[\text{H}]$ ; the 2-D modeling predicts a modest increase in  $\text{N}_2^*$  emission intensity over the range  $0.8 \leq P \leq 1.5 \text{ kW}$ , in accord with experimental observation (see Figure 8a), as a result of the increasing  $\text{N}_2(\text{C} \leftarrow \text{X})$  EI excitation rate.

In the case of the  $\text{NH}_3/\text{H}_2$  plasma, however, this same increase in  $P$  causes a modest decrease in  $\{\text{NH}(\nu=0)\}$ , a smooth increase in the  $\text{N}_2^*$  emission intensity, and no clear change in  $\text{NH}^*$  emission. As noted earlier, the predicted  $\{\text{NH}(\nu=0)\}$  values with the  $\text{NH}_3/\text{H}_2$  plasma far exceed those observed experimentally, but the present modeling succeeds (qualitatively at least) in reproducing the observed decrease in  $\{\text{NH}(\nu=0)\}$ . This is attributable to the order of magnitude decrease in  $[\text{NH}_3]$ , particularly in the hot plasma region, as a result of a 3-fold (over the entire reactor volume) increase in  $[\text{H}]$ , which promotes the conversion of  $\text{NH}_x$  to  $\text{N}_2$ .

**4.2.2. Pressure Dependences.** As eq 12 shows, decreasing  $p$  at constant  $P$  could be accommodated by (i) a compensating change in  $V_{\text{pl}}$  (i.e.,  $V_{\text{pl}} \sim 1/p$ ), with no effect on  $E/N$ ,  $T$ , or  $n_e$ ; (ii)  $V_{\text{pl}}$  remaining constant with increasing  $E/N$  and  $n_e$ ; or (iii) a combination of both effects. Inspecting the model outputs for the 1.2%  $\text{N}_2/\text{H}_2$  mixture under base conditions and at  $p = 80 \text{ Torr}$  suggests that scenario (iii) is most applicable. Reducing  $p$  from 150 to 80 Torr is predicted to result in a  $\approx 35\%$  increase in  $V_{\text{pl}}$  (from  $\approx 74$  to  $\approx 100 \text{ cm}^3$ ), with corresponding increases of  $\approx 30\%$  in the maximal  $n_e$  (from  $2.2 \times 10^{11}$  to  $2.8 \times 10^{11} \text{ cm}^{-3}$ ) and  $\approx 10\%$  in  $T_e$  (from 1.24 to 1.36 eV) at the plasma center. The maximal value of  $X(\text{H})$  is reduced by  $\approx 45\%$ , from 7.3% to 4.0%, reflecting the  $\sim [\text{H}_2]^2$  dependence of the thermal dissociation source term.

The present modeling of the  $\text{N}_2/\text{H}_2$  plasma captures the observed increases in  $\{\text{H}(n=2)\}$  and  $\{\text{NH}(\nu=0)\}$  upon increasing  $p$ , as depicted in Figure 5b. The calculated  $z$ -dependent  $\{\text{NH}(\nu=0)\}$  profile at lower  $p$  is also flatter, in accord with the CRDS measurements (not shown). The model also provides a rationale for the very different  $p$  dependences of the  $\text{N}_2^*$  and  $\text{NH}^*$  emission intensities displayed in Figure 8b. These intensities are sensitive to the  $\text{N}_2(\text{C} \leftarrow \text{X})$  and  $\text{NH}(\text{A} \leftarrow \text{X})$  EI excitation rates. The former, for example, is given by the product  $k_e(\text{N}_2(\text{C} \leftarrow \text{X})) \times n_e \times [\text{N}_2(\text{X})]$ , where the EI rate coefficient for  $\text{N}_2(\text{C} \leftarrow \text{X})$  excitation is derived from the calculated EEDF,  $k_e = 2.1 \times 10^{-8} \times \exp(-11/T_e[\text{eV}]) \approx 3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  for a typical value of  $T_e = 1.25 \text{ eV}$ . The  $\text{N}_2^*$  versus  $p$  trend displayed in Figure 8b shows that the net effect of the decreases in  $n_e$ ,  $T_e$  (and thus  $k_e$ ) with increasing  $p$  more than outweigh the (linear) increase in  $[\text{N}_2(\text{X})]$ . The  $\text{NH}(\text{A} \leftarrow \text{X})$  EI excitation frequency  $k_e(\text{NH}(\text{A} \leftarrow \text{X})) \times n_e$  will also decline with increasing  $p$ , but the  $\text{NH}^*$  emission is seen to increase and then plateau at  $p \approx 150 \text{ Torr}$ . This reflects the previously noted greater than linear increase of  $[\text{NH}(\text{X})]$  (and other  $\text{NH}_x$  species) due to the near quadratic dependence of  $X(\text{H})$  with  $p$  in the hot plasma region.

The foregoing discussion excludes any possible contribution to the observed  $N_2^*$  emissions from EI pumping of molecules in any state other than the ground state on number density grounds;  $k_e(N_2(C \leftarrow A3))$  is estimated to be an order of magnitude larger than  $k_e(N_2(C \leftarrow X))$ , but this difference is overwhelmed by the concentration difference ( $[N_2(A3)]/[N_2(X)] < 10^{-5}$ ) in the hot plasma region. The  $N_2(C \leftarrow X)$  excitation must be balanced by  $N_2(C \rightarrow B)$  radiative decay and collisional quenching. Probe calculations suggest that the latter must dominate in order to reproduce the observed smooth spatial  $N_2^*$  emission profiles. The only feasible quencher (on concentration grounds) is  $H_2$ , for which Pancheshnyi et al.<sup>41</sup> report a suitably large  $N_2(C^3\Pi_u) + H_2$  quenching rate coefficient  $k_q > 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (at 295 K).

Notwithstanding the previously noted limited agreement between the experimental data and model outputs for the MW activated  $NH_3/H_2$  gas mixtures, the 2-D model also succeeds in reproducing the near independence of  $\{NH(\nu = 0)\}$  with  $p$  (Figure 5b), reflecting the alternative  $NH_x$  source term when using  $NH_3$  as the nitrogen source gas, and accounts for the  $p$ -dependent  $N_2^*$  and  $NH^*$  emission intensities shown in Figure 8b. The observed  $p$ -dependence of  $N_2^*$  is very similar to that seen with the  $N_2/H_2$  plasma, for the same reasons. The  $NH^*$  emission from the  $NH_3/H_2$  plasma, in contrast, declines with increasing  $p$ , which is as expected for the product of a (nearly  $p$ -independent)  $NH(X)$  density and an  $NH(A \leftarrow X)$  EI excitation rate coefficient that declines with increasing  $p$ .

## 5. SUMMARY AND CONCLUSIONS

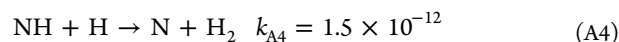
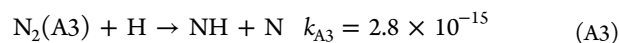
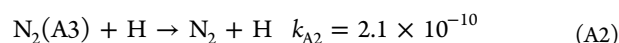
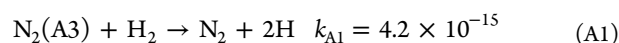
Small additions of  $N_2$  to MW-activated  $CH_4/H_2$  gas mixtures used in diamond CVD have been shown to enhance the material growth rate and influence the surface morphology,<sup>2–6</sup> but a complete mechanistic explanation for such behavior has yet to be determined. Here, we have addressed dilute  $N_2/H_2$  and  $NH_3/H_2$  microwave plasmas operating under CVD-relevant regimes of gas temperature and pressure, which have otherwise received little attention thus far. The present work can therefore be considered a prerequisite for any subsequent study of N-containing  $CH_4/H_2$  plasmas, such as those that are used in many diamond CVD reactors. Our investigation has involved three main aspects: (i) CRDS measurements, yielding spatially resolved absolute column densities of  $H(n = 2)$  atoms and  $NH(X)$  radicals, as functions of gas pressure  $p$ , input power  $P$ , and mole fraction of nitrogen in the source gas  $X_0(N)$ , (ii) OES measurements of the relative densities of  $H(n = 3)$  atoms,  $NH(A)$  radicals, and triplet  $N_2$  molecules, with respect to the same process conditions; and (iii) complementary 2-D ( $r, z$ ) coupled kinetic and transport modeling for the same process conditions, including consideration of variations in both the plasma parameters (e.g.,  $T_e$ ,  $T$ ,  $n_e$ , and power density  $Q$ ) and the overall chemistry.

Comparisons between experimental measurements and model outputs have provided refinements to the prior understanding of N/H plasma-chemical reactivity, with the proposed scheme now able to demonstrate the interconversion between  $NH_x$  ( $x = 0–3$ ) and  $N_2H_x$  ( $x = 0–4$ ) species, and its dependence on process conditions and location within the reactor. We have highlighted the essential role of metastable  $N_2(A^3\Sigma_u^+)$  molecules (formed by electron impact), and their hitherto underappreciated reactivity with H atoms, in converting the  $N_2$  process gas into reactive  $NH_x$  ( $x = 0–3$ ) radical species. We have also illustrated the much more extensive  $NH_x$  spatial distributions prevailing in MW-activated

$NH_3/H_2$  plasmas, and the importance of surface-mediated  $NH_x$  loss processes in establishing the measured radical densities in the case of the  $NH_3$  feedstock. The overall result is that we are now satisfactorily able to rationalize the observation that measured  $NH$  column densities differ by less than a factor of 2 between  $N_2/H_2$ - and  $NH_3/H_2$ -based MWPACVD processes operating under base conditions with the same nitrogen atom input mole fraction, though the difference is larger at lower  $p$  and/or  $P$ . An important additional finding in the CVD context is that N atoms are, by an order of magnitude, the dominant reactive nitrogenous species in the near-substrate region under the present conditions.

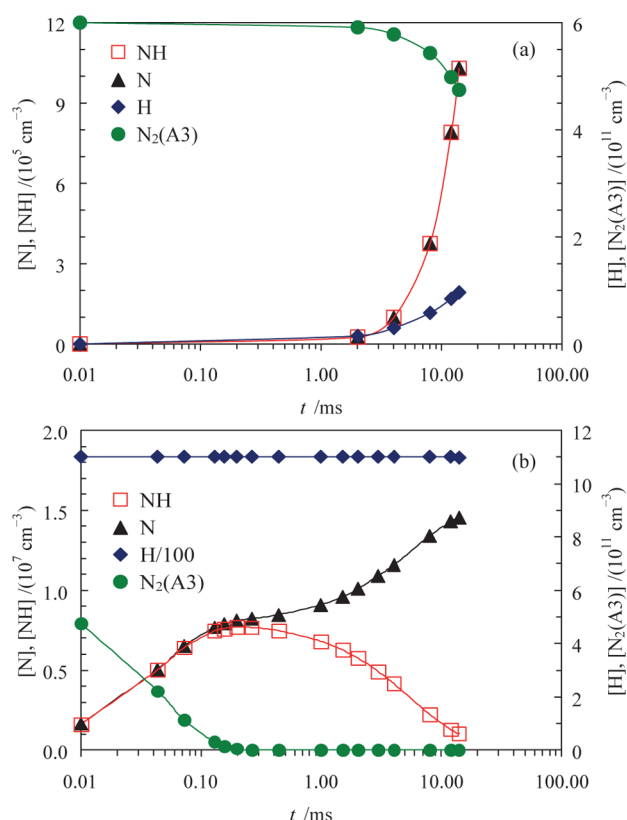
## ■ APPENDIX

The earlier fast discharge flow studies of reactive conversions in  $N_2(A3)/H_2/Ar$  and  $N_2(A3)/H/H_2/Ar$  gas mixtures involved monitoring relative (and, with appropriate calibration experiments in many cases absolute) H atom,  $N_2(A3)$  molecule and  $NH(X)$  and  $NH_2(X)$  radical concentrations downstream of the mixing region.<sup>38</sup> Data relevant to the current study have been simulated using the following minimalist reaction scheme (with respective rate coefficients  $k_{Ai}$  ( $\text{cm}^3 \text{ s}^{-1}$ ) at the experimental temperature  $T = 295 \text{ K}$ ):



These rate coefficients were drawn from various sources:  $k_{A1}$  and  $k_{A2}$  from experimental data surveyed in the Herron evaluation,<sup>39</sup>  $k_{A4}$  from the combined experimental and theoretical study of reaction A4 by Adam et al.,<sup>42</sup> and  $k_{A3}$  derived from present study. This value of  $k_{A3}$  does not contradict the conclusion of the Ho and Golde study,<sup>43</sup> given it is so much smaller than  $k_{A2}$  ( $k_{A3} \approx 1.3 \times 10^{-5} \times k_{A2}$ ). The simple mechanism (A1)–(A4) is able to replicate many of the features observed in the fast discharge flow experiments, e.g., the lack of any discernible increase in  $[NH]$  at the measurement time,  $t = 14 \text{ ms}$ , upon introducing H atoms at a concentration  $[H] = 1.1 \times 10^{14} \text{ cm}^{-3}$  ( $X(H) = 0.17\%$ ). The fact that the observations are made downstream, after a user-selected time delay  $t$ , is crucial to the interpretation. As Figure 14 shows, reaction A3 leads to an initial increase in  $[NH]$ , which has then declined precipitously by the time of the measurement through reaction A4 with the high concentration of H atoms.

Though appealing, this simple analysis of the prior data may well be deficient in detail. For example, we note that the present calculations return  $[H]$  concentrations in the experiments using the 0.001%  $N_2(A3)/25\% N_2/2.3\% H_2/Ar$  gas mixture (i.e., without any deliberate H atom addition, Figure 14a) that are an order of magnitude larger than the measured value ( $[H] \sim 10^{10} \text{ cm}^{-3}$ , per ref 38). Such a low  $[H]$  is inconsistent with the  $k_{A1}$  value assumed here and in ref 38, but we recognize that the experimental  $[H]$  values could be underestimated as a result of, for example, H atom recombination on the Pyrex tube surface.



**Figure 14.** Evolution of selected species concentrations in the fast discharge flow experiments assuming the simple reaction scheme A1–A4 for a 0.001%  $N_2(A3)/25\% N_2/2.3\% H_2/Ar$  mixture (a) without and (b) with the addition of atomic hydrogen at a mole fraction  $X(H) = 0.17\%$ .

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### Notes

The authors declare no competing financial interest.

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